

# A LABORATORY OUTLINE OF COLLEGE CHEMISTRY

BY

ALEXANDER SMITH

PROFESSOR OF CHEMISTRY, AND HEAD OF THE DEPARTMENT,  
COLUMBIA UNIVERSITY



LONDON

G BELL AND SONS, LTD

1919



## PREFACE

THE present Laboratory Outline follows the order of topics in the second edition (1916) of the author's *General Chemistry for Colleges*. A number of new experiments, such as those on hard water, colloids, foods, baking powder, dyeing, and Bunsen's film and match tests, have been introduced.

It is not intended that the whole of the experiments should be performed by any one class. The sub-division into small paragraphs will make omissions easy. The choice will depend upon the preferences of the instructor and upon the purpose for which the course is being given.

The weakest point in most, if not in all, forms of education is the resulting lack of a sense of quantity. A few quantitative experiments will have no effect, if hundreds of other experiments are performed without reference to this feature. The quantitative sense must be cultivated until it is used habitually in all connections. The students should be urged to note the quantity of each material taken, and the concentration of each reagent used (normal, as a rule), and consciously to add equivalent amounts. Where a smaller amount, or an excess, is required, the fact is specified in the directions. In adding sodium hydroxide solution to alum, for example, not one student in a hundred will avoid adding an enormous excess, before studying the result. If the student continues in chemistry, training of the sense of quantity will be of immense value. If he does not pursue chemistry, as the majority do not, the training will still be most useful to him in other studies and, in business, will make all the difference between success and failure.

The list of reagents, in the Appendix, indicates concentrations which are convenient

This outline may be employed also along with the *Introduction to Inorganic Chemistry*. To facilitate this, a table at the end gives the equivalents of the references to pages in the *College Chemistry* which are used exclusively in the text of the outline.

ALEXANDER SMITH

# CONTENTS

CHAPTERS	PAGES
GENERAL DIRECTIONS	1
I MANIPULATION	3
II CHARACTERISTICS OF CHEMICAL PHENOMENA	10
III OXYGEN	16
IV HYDROGEN	20
V COMPOSITIONS AND FORMULÆ OF SUBSTANCES	25
VI WATER	33
VII MOLECULAR AND ATOMIC WEIGHTS	36
VIII SOLUTION	43
IX HYDROGEN CHLORIDE AND CHLORINE	50
X CHEMICAL EQUILIBRIUM THE HALOGENS	55
XI DOUBLE DECOMPOSITION HYDROGEN PEROXIDE	66
XII IONIZATION AND INTERACTIONS OF ACIDS, BASES AND SALTS	70
XIII SULPHUR	82
XIV OXYGEN ACIDS OF THE HALOGENS	98
XV THE ATMOSPHERE, NITROGEN, AMMONIA	104
XVI OXIDES AND OXYGEN ACIDS OF NITROGEN	110
XVII PHOSPHORUS	120
XVIII OXIDES OF CARBON HYDROCARBONS	125
XIX CARBOHYDRATES AND SUBSTANCES DERIVED FROM THEM	132
XX ORGANIC ESTERS AND SALTS COLLOIDS SOAP FOODS	137
XXI SILICON AND BORON	143
XXII METALLIC ELEMENTS OF THE ALKALIES	147
XXIII METALLIC ELEMENTS OF THE ALKALINE EARTHS	157
• XXIV COPPER AND SILVER	164
XXV MAGNESIUM, ZINC, CADMIUM, MERCURY	170
XXVI ALUMINIUM, DYING, TIN, LEAD	176
• XXVII ARSENIC, ANTIMONY, BISMUTH	182
XXVIII FILM TESTS AND MATCH TESTS	186
XXIX CHROMIUM, MANGANESE	191
XXX IRON, COBALT, NICKEL	195
APPENDIX	198



## GENERAL DIRECTIONS

### NOTES 1-17

Read the "Regulations" posted in the laboratory. Read also, attentively, the following notes.

**Note 1** — Provide yourself with a **note-book** and make a careful permanent record immediately after each experiment. Enter the numbers and titles of the paragraphs of the outline systematically. State (1) what you did, if anything beyond the directions, but do not copy the printed directions themselves, (2) what you observed, (3) what conclusions you drew. A sketch of the apparatus will enable you to recall the circumstances of the experiment, if later reference to it is necessary. This note-book, when called for, is to be handed in for inspection.

The directions have been expressed with the utmost care and brevity. Every word is significant. Italics are therefore nowhere employed for the purpose of emphasis.

**Note 2** — Whenever an **interrogation point** or a **direct question** appears, a corresponding note should appear in the note-book. The "(?)" indicates something to be observed and recorded.

**Note 3** — The very numerous **questions** asked in the course of this outline are intended to be answered, not by speculation, but by careful observation and reasoning based on the results of this. Very often the student will find it necessary to devise and carry out further experiments of his own before a satisfactory answer is obtained. When a question occurs to you, endeavor by reflection and study to answer it yourself before consulting an instructor.

**Note 4** — In many cases the work outlined could not in itself furnish the basis for an answer, and fuller investigation of the point would require work beyond the time or ability at the disposal of the beginner. Such questions are distinguished by an [R], indicating that Reference to some authority (lecture, book, or assistant) must be made. The number following the R is that of the page in Alexander Smith's *General Chemistry for Colleges* (Second Edition), where the necessary information may be obtained. The authority should be consulted, however, only after the experiments have been made and the notes written up as far as possible.

**Note 5** — When a chemical change has been observed the **equation** should always be given in the notes, but an equation alone is never a sufficient record.

**Note 6** — Where the word [Instructions] appears, consult the instructor before going further.

*Note 7* — In quantitative experiments, marked [Quant], use the finer balance, in all other cases the rough scales in the laboratory

*Note 8* — The expression [Storeroom] indicates that the necessary apparatus is not included in the individual outfits

*Note 9* — When the word [Hood] appears, the operation is not to be conducted in the open laboratory. The apparatus must be at once placed close to the desk-ventilator, or be transferred to the hood

*Note 10* — Where exact quantities are not indicated, very small amounts of solutions (1 c c or less) should be taken. This advice is given, partly to secure saving of material, but chiefly to avoid the waste of time which working with large quantities always entails

*Note 11* — To obtain the necessary chemical substances, if the chemicals are not furnished in "kits" to each student, do not carry the bottles from the side-shelf to the desk. Bring a clean test-tube for liquids and a watch-glass for solids. For the latter, a piece of the paper, provided near the side-shelf, may also be used. When too much of any reagent has been taken, do not return it to the bottle

*Note 12* — The chemicals, if on a side-shelf, are divided into two sets, each arranged alphabetically according to the scientific names. The first set consists of solids in small bottles, the second of liquids. The bottles and their places are numbered consecutively to facilitate accurate replacement, and scrupulous care must be taken not to disarrange them. Read the labels attentively, as there are frequently several kinds of the same substance (e g, pure, and commercial, dilute, concentrated, and normal)

All materials are supplied through the storeroom service. Do not therefore take bottles, when found empty, to the instructor, but to the storekeeper for refilling

*Note 13* — The expression [From Instructor], however, indicates one of a few special substances for which the student must apply to an instructor

*Note 14* — The bottles on the desk, if there are any, contain certain substances which are frequently used. These substances will not be found on the side-shelf

*Note 15* — When any acid gets upon the clothing, apply ammonium hydroxide solution at once

*Note 16* — Burns, whether caused by contact with hot objects, by acids, or by corrosive liquids like bromine, are rubbed gently with a paste of sodium-hydrogen carbonate and water. All burns, save the slightest, must afterwards be dressed with an aqueous solution of boric acid (half-saturated) to prevent infection. Obtain the assistance of an instructor

Cuts must be washed in running water and dressed with boric acid as above, or with lanolin containing 2 per cent of boric acid

*Note 17* — All students work independently, except where coöperation of two students is expressly directed



# LABORATORY OUTLINE

## CHAPTER I

### MANIPULATION

**The Outfit of Apparatus** As articles missing or found imperfect when the course is completed will be charged for, check the outfit of apparatus carefully by comparison with the list. To do this, put all the articles on the top of the desk and make a mark on the margin of the list opposite to the names of such as you are able to identify, at the same time returning the article to the cupboard or drawer. With the assistance of an instructor, the remaining, unfamiliar articles can then be checked also.

#### 1 Instructions

*a* Read the general directions and notes preceding this chapter very carefully, and do not fail to observe them.

*b* The number of blast-lamps and balances being limited, the whole class cannot perform the experiments in this chapter simultaneously in the order given. The order is, in any case, a matter of indifference. Two students from the group under each assistant will begin with glass-working (3) or weighing (5 and 6 *a* and *b*). The other students will meanwhile perform 2, and 6 *d* at the desks.

*c* Record in the note-book the results of 2, 3, 5, and 6 only.

#### 2 Bunsen Burner

*a* Attach the Bunsen burner by means of rubber tubing to a gas connection, close the air-holes at the base and light. Now open the air-holes gradually and note the effect upon the flame (?). Close the air-holes again, and hold a porcelain dish

in the flame What is deposited on the dish? When using the burner for heating purposes, always regulate the air supply so as to get a noiseless, non-luminous flame

b Determine the structure of the non-luminous flame Which parts are relatively hotter, and which cooler? This may be ascertained by holding one match across the flame 1.5 cm from the bottom (?), and another near the top (?) Make a sketch showing the real form of the flame (?) Where should you hold an object in the non-luminous flame, in order to get the greatest heating effect? Insert one end of a narrow glass tube into the inner cone, and ascertain whether any unburnt gas ascends through the tube (?)

Which region is deficient in oxygen and which has an excess? The former is called the reducing, the latter the oxidizing region

Sometimes the flame descends and burns noisily at the bottom of the tube This back-fire happens when too much air is admitted Shut off the gas, close the air-holes, turn the gas on again, and relight

c Place in a watch-glass [Note 12, p 2], a small quantity of borax\* (sodium tetraborate) Heat your platinum wire, which has been inserted into the fused end of a glass rod, and immerse the glowing end of the wire in the borax Use the wire in straight condition, without any loop Now, hold the wire in the flame, observe the behavior of the borax, and explain [R 465 See Note 4, p 1] (?) The bead must be small to avoid its dropping off

d Bring the hot borax bead in contact with a minute particle of manganese dioxide [Notes 11 and 12], heat in the flame near the outer edge until the particle has dissolved, and observe the color of the bead when cold (?) If the bead is opaque, too much of the dioxide has been taken melt the bead, throw it off, and start again

\* In this Outline the common, or popular names are often used intentionally The systematic names must, in such cases, be found by the student [R]

e Cut off the gas supply until the flame is about 6 cm. in height. Close the air-holes until a luminous point appears at the apex of the inner cone, and hold the bead containing the manganese dioxide steadily in this luminous (reducing) portion. Before withdrawing the bead, lower it into the inner cone of unburnt gases to cool. Observe the color of the bead (?).

f Reheat the bead in the oxidizing part of the flame (?).

3 **Glass-Working** [Blast-Lamp Table Instructions, and Note 18, below]

a Cut a small piece off the wide soft glass tubing and make a test-tube of it.

b Make a test-tube of hard (?) [R 194] glass.

c Connect two pieces of narrow glass tubing to make a longer piece.

d Make a T-tube by connecting two pieces of narrow glass tubing at right angles to each other.

*Note 18* — To cut narrow glass tubing make a slight, transverse scratch with the triangular file. Hold the tubing so that the points of the thumbs are together opposite to the scratch, and press forward with the thumbs so as to bend the tube away from this mark. Wide tubing may be cut by making a deep scratch completely round the tube and starting the crack by touching with the red-hot end of a glass rod. Other methods may be shown by the instructor.

Always round off (**fire-polish**) the sharp edges of freshly cut tubes by softening them in the Bunsen flame (why do the edges become rounded?). In the case of test-tubes, and other tubes of wide bore in which coils are to be inserted, the mouth must be strengthened and rendered fit for receiving the coil. To accomplish this, heat the edge in the flame and spread it slightly, but uniformly, by rotating it in a pointed piece of charcoal, or by turning outward the softened edge with the reverse end of a file.

In making test-tubes and in connecting pieces of tubing, distend the softened parts by blowing immediately before allowing to cool, otherwise cracks are likely to appear.

To bend glass tubing, never use the ordinary Bunsen flame (why? Note 3). Place the wing-top on the burner, and use the resulting flat, luminous flame, of fish-tail form. Hold the tubing lengthwise in the flame, not across it (why?), turning the tube slowly round its axis to insure uni-

form heating Keep the tube straight until it is soft enough to bend by its own weight Finally, do not actually make the bend while the tube is in the flame, but after removal from it (why?)

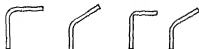


Fig 1

Hold a piece of tubing in the Bunsen flame, without rotating the tube, and bend it while it is in the flame (?) Compare the bend with one made in the proper way (Fig 1) and account for the difference (?)

**4 Construction of a Wash-Bottle** Select a good cork which will fit the mouth of the largest flask and soften it by rolling under the foot upon the floor while pressure is cautiously applied Bore two parallel holes with the cork-borer, and smooth them by means of a rat-tail file [Note 19, below] Bend two pieces of glass tubing as indicated in Fig 2 [Note 18], fire-polish their edges and insert them in the openings in the cork Make the nozzle by softening a piece of glass tubing in the Bunsen flame, drawing it to capillary dimensions after removal from the flame (Fig 3), cutting (6-8 cm long), and fire-polishing Connect the nozzle by means of a short piece of rubber tubing Test the apparatus



Fig 2



Fig 3

to see that it is air-tight [Note 20] Finally, fill the flask with distilled water [Note 21]

*Note 19* — The cork borer is usually made of brass, and the edge is easily turned Form the habit of examining the edge and freshening it by cautious application of a triangular file [Instructions Note 6] every time it is to be used Do not hold the cork against the table while boring, as the edge of the tool may be ruined Hold the cork in the hand and bore from the narrow end, with care, exactly parallel to the axis If the cork and borer are rotated round their axes and the edge is fresh, very little force will be required Clear the core of cork out of

the cork-borer, after use, by means of the hon rod. The borer is purposely chosen so as to be smaller than the tubing. Its use thus permits the enlarging and smoothing of the hole with the rat-tail file until a perfectly fitting bore has been made.

*Note 20* — Before use, every piece of closed apparatus employed in this and all succeeding experiments must be **tested for air-tightness**, and rendered perfectly air-tight. In this instance place in the flask enough water to cover the lower end of the longer tube and transfer the rubber connection to the shorter glass tube and close it with a clamp. Now, blow through the longer tube so that a few bubbles of air pass into the flask. If the apparatus is air-tight the water will rise in this tube when the mouth is withdrawn and will remain in an elevated position. If the water gradually sinks to its former level, the apparatus is not air-tight. Examination of the holes in the cork may show defects, which can be remedied only by boring a fresh cork more carefully. If the cork itself contains pores, these may often be closed by thorough wetting. Do not on any account employ paraffin or sealing-wax to patch defective places in a cork, use a fresh one.

*Note 21* — **Distilled water** is to be used for making solutions and for rinsing glassware (why?) Common water is to be used for all other purposes.

**5 Use of the Simple Balance** [Instructions Quant.] By turning the screw attachment in front of balance case, release the beam and pans, allowing the beam to swing. Observe the excursions made by the pointer. Divide by two the total divisions covered by the pointer in one full swing, and count off from either end of the swing the divisions which this number designates, thus finding the position of the true zero point. The beam must swing freely during the observation. the zero is never to be read with the beam at rest.

This observed zero point may be a little to the right or to the left of the marked zero. Note down its distance, in scale divisions, from the marked zero. If it lies to the right, prefix to the number of divisions the minus (—) sign, if to the left, the plus (+) sign. The zero of any one balance changes, and must be redetermined every time a weighing is made.

Place a 10 g. weight in each pan [Note 22, below], and determine the zero as before. Add the 01 g. weight to the right-

hand pan, and find the reading about which the pointer now oscillates. The difference in reading between this point and the last determined zero point gives the deflection due to the 01 g weight. It may be used for estimating weights less than 01 g. Thus, suppose the 01 g weight causes a deflection of 5 divisions to the left (+5). When some body is being weighed, if the deflection is +1, then  $\frac{1}{5}$  of the 01 g or 002 g, must be added to the sum of the weights.

*Note 22* — Great care must be taken in the use of the balance and weights. The pans of the former must be let down upon their supports when not in use and every time weights or other objects are to be added or removed. All objects to be placed upon the pans must previously be carefully cleaned and dried. Solids are placed upon a watch-glass or upon a piece of glazed paper, and never directly upon the pans. The weights must be lifted from their case by means of forceps, never by the fingers. They are usually placed on the right-hand pan, the objects to be weighed on the left.

*Note 23* — In reckoning results, count first by the places vacant in the box, and check by counting the weights themselves. This will enable you to avoid the commonest error in weighing, namely, miscounting the weights. Finally record the weights in the note-book, and never upon loose sheets of paper, as loss of the latter will necessitate a repetition of the entire experiment.

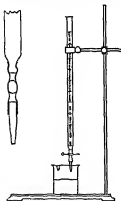


Fig. 4

## 6 Measuring Vessels [Quant.]

*a* Fit a burette (Fig. 4) with a short piece of rubber tubing and glass nozzle (see 4). The withdrawal of liquid from the burette is regulated by a pinch clamp upon this rubber connection, or by placing a small piece of glass rod (with fine-polished edges) in the middle of the rubber tubing to choke the bore (Fig. 4).

In this latter case, pinching the tubing surrounding the glass rod will permit the liquid to flow at any desired rate from the nozzle.

b Support the burette upon a ring-stand by means of a clamp. Now fill the burette with distilled water, drawing off a portion to insure the complete removal of air from the rubber tubing and nozzle. The last bubble of air may be removed by turning the nozzle upward while the water is allowed to flow. Read the height of water by observing the lower side of the meniscus (Fig. 5) and estimate to tenths of a division.



Fig. 5

Clean and dry a small beaker carefully and weigh it. [Quant.] Allow 10-20 c.c. of the distilled water to run from the burette into the beaker, read the new level of the water, and ascertain the volume taken by subtracting the readings. Weigh the beaker again and ascertain the weight of the water by subtraction. Calculate from your figures the weight of 1 c.c. of water. The result is the density of water. Keep the beaker and contents for use in c.

c Place some distilled water in the graduated cylinder and read its volume. Pour about 10 c.c. of this water into the beaker (already partly filled with water), read the volume of the remainder, and find by subtraction the volume poured out. Now weigh the beaker once more and find the weight of this water by subtracting the previous weight. Calculate the weight of 1 c.c. of water.

Is measuring volume by burette or by cylinder more accurate and why?

d Measure by means of the cylinder, roughly, the volumes of water your flasks and beakers hold, and record the figures. Fill the vessels to a convenient height for use, and not to the brim.

**7 Physical Properties, Attributes, and Conditions.** Make a list of the physical properties [R. 19] of water, so far as you have observed them (?).

Which attributes [R. 20] were employed in 6 b and c?

What conditions [R. 20] (temperatures and pressures) existed while 6 a and b were performed?

## CHAPTER II

### CHARACTERISTICS OF CHEMICAL PHENOMENA

#### 8 Qualitative Study of Chemical Phenomena

a Rub a pinch (about 0.5 g) of powdered roll sulphur with a very small globule of mercury (use the dropper) in a mortar (?) When the mass has been intimately ground together for about five or ten minutes and no particles of mercury are longer observable, place it in a dry test-tube and add about 3 c.c. of carbon disulphide [CARE! Keep away from flames], a solvent for the free sulphur. Shake well (do not apply heat) and then pour off the clear solution into the sink [Hood. Note 25, below]. Repeat, shaking well and pouring away the clear liquid. Continue this operation until a sample of the decanted liquid fails to give any sulphur by spontaneous evaporation upon a watch-glass. What is the product remaining in the tube [R 535]? By means of a few c.c. of carbon disulphide wash this product out upon a filter paper [Note 24, below] and allow it to dry. To show the composition of this substance place it in a small, clean, dry test-tube and heat strongly over a flame. What odor is noticed at the mouth of the tube? What product is found to sublime upon the walls of the test-tube? Rub the sublimate with a glass rod (?) What evidence of chemical change have you noticed in the above experiment?

The mortar may be cleaned by placing in it a few drops each of hydrochloric acid and of nitric acid.

*Note 24* — Cut from a sheet of **filter paper** a piece 7 cm (3 inches) square. Fold the square twice in directions at right angles to one another, so as to obtain a square of one-fourth the previous area. Cut off the loose corners with scissors so that a quadrant is formed. Open the folded paper



so that a cone is produced (Fig 6), and place the cone in a dry glass funnel. Smaller or larger pieces of paper are taken according to the amount of the precipitate or of the liquid to be filtered, the smallest size that will serve the purpose being preferred. The funnel must be chosen so that the filter paper, after being tumbled and placed in position, does not quite reach the edge, much less project above it. While in use, the funnel is placed in a ring on the stand, and is not to be held in the hand.

*Note 25* — Pour away all ill-smelling substances, like carbon disulphide, in the sink in the hood and not in the ordinary sinks or jars.

*b* Make separate lists of the physical properties of mercury, of sulphur, and of mercuric sulphide, as you have observed them (?). Are mercury and sulphur the components, or the constituents of mercuric sulphide?

*c* Gunpowder is made from saltpeter (potassium nitrate), sulphur, and charcoal. Take specimens of these three substances, and examine them with respect to properties which can be used for recognition and separation [R 11, 12, 19], such as appearance and solubility in various solvents. Try the solubility of each in distilled water and in carbon disulphide, using in the latter case thoroughly dried (why?) test-tubes [Notes 25 and 26]. Do not judge of solubility by the eye, but filter the mixture [Note 24], catch a few drops of the liquid on a watch-glass, evaporate, and see whether there is any greater stain on the glass than the pure solvent would itself have left. The taste (?) of the saltpeter is a characteristic property.

Now place about 1 g of gunpowder in a large test-tube and add 5-10 c c of water. Shake well (after closing the test-tube with the thumb), warm gently, and filter [Note 24]. Evaporate

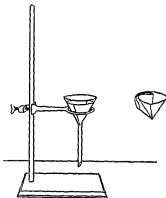


Fig 6

the filtrate upon a water bath or over a beaker of boiling water (Fig 7) Describe and name the residue (?) Dry (why?) the

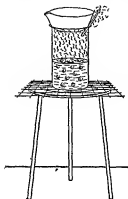


Fig 7

filter paper and its black contents over a radiator or in a drying oven Shake the dried product with cold carbon disulphide in a dry [Note 26] test-tube, filter, and allow the filtrate to evaporate [Hood] spontaneously (?) What remains upon the paper?

Did any chemical change occur during the manufacture of gun-powder? Are the three substances components or constituents of gun-powder? Is the latter a mixture or a compound?

Why are the ingredients of gun-powder pulverized so finely and mixed so intimately?

*Note 26* — To dry test-tubes or flasks quickly, after recent washing, warm them slightly in the Bunsen flame, connect with the air supply of a blast-lamp a piece of glass tubing long enough to reach to the bottom of the vessel, and allow a gentle stream of air to flow through the tube and vessel

### 9 Law of Definite Proportions\* [Quant R 17]

Obtain two pieces of pure lead of different sizes, about 0.5 g and 0.6 g respectively Clean and dry two evaporating dishes, taking care to remove any paper labels which may be, attached to them, and weigh each with care [Quant, balance] Place one piece of the lead in each and weigh again Record the results in the form shown below The difference will give

\* Before beginning, always endeavor to ascertain the object of each experiment By this means confused work and much waste of time will often be avoided, and significant facts to be observed and recorded will not escape notice Consider, first, carefully the title, as it will usually indicate the object of the exercise If the title is not at once fully understood, look up the topic in a reference book before going further

the exact weight of the lead. Be careful in your notes, and in handling, to distinguish the dishes from one another.

Dilute 7 c c of pure, concentrated nitric acid with 14 c c of water in the graduated cylinder and add to the lead in each dish 10 c c of the diluted (1/2) nitric acid. Cover each dish with a watch-glass, convex side downward, and set upon the water bath. An extra Bunsen burner [Storeroom] and two beakers containing water may be used as baths, as in Fig 7 [Hood]. A match inserted between the dish and the beaker permits escape of the steam and prevents the possible upsetting of the dish by the vapor. When the action is over, and the lead has entirely disappeared, rinse the lower surface of each watch-glass into the dish by means of a little water from the wash-bottle. Then add to the contents of each 5 c c of pure dilute hydrochloric acid. This causes the precipitation of a compound of lead and chlorine whose weight is next to be determined. To accomplish this, the water and other substances present (except the lead chloride) being all volatile, the mixture is dried by evaporation on a water bath. When the contents of the dishes are dry, moisten the contents of each with 2 c c of pure, concentrated hydrochloric acid and dry once more. Now transfer the dishes, one at a time, to the clay triangle supported on the ring-stand, and heat the whole residue cautiously with a small Bunsen flame. Watch it narrowly and do not allow any of it to melt. When the dishes are cold, weigh each again with care. The increase in weight over the previous value in each case gives the weight of chlorine which has combined with the known weight of lead.

Dish No 1    Dish No 2

Wt of dish with lead (silver)

Wt of dish, empty

Wt of lead (silver)

Wt of dish with lead (silver) chloride

Wt of dish with lead (silver)

Wt of chlorine

# 14 CHARACTERISTICS OF CHEMICAL PHENOMENA [§ 10

	Dish No 1	Dish No 2
Wt of lead (silver)		
Wt of chlorine		
Wt of lead (silver) chloride		
Per cent lead (silver) ( $x$ )	No 1	No 2
Per cent chlorine ( $x'$ )		

Calculate from each of the two sets of data the percentage of lead ( $x$ ) and of chlorine ( $x'$ ) in lead chloride

$$\frac{\text{Wt of lead used}}{\text{Wt of lead chloride}} \times 100$$

$$\frac{\text{Wt of chlorine found}}{\text{Wt of lead chloride}} \times 100$$

Compare the results of the two measurements and interpret (?)

## 10 Law of Definite Proportions\* [Quant R 17]

a To secure almost ideal results, two pieces of pure silver foil of about 0.5 g and 0.6 g should be substituted for the lead in 9. Record the weights as shown above

Dilute 5 c.c. of concentrated nitric acid with 5 c.c. of distilled water in the graduated cylinder and add to the silver in each dish 5 c.c. of the diluted (1:1) acid. When the action is over, and the cover-glasses have been used, as in 9, add 2 c.c. of pure, dilute hydrochloric acid to the contents of each dish. This causes precipitation of a compound of silver and chlorine. Evaporate the liquids to dryness [Hood] and heat the residues at once until signs of melting are seen. Weigh each dish. The increase in weight over the previous value in each case gives the amount of chlorine which has combined with the known weight of silver.

Calculate from each of the two sets of data the percentages of silver ( $x$ ) and of chlorine ( $x'$ ) in silver chloride

$$\frac{\text{Wt of silver used}}{\text{Wt of silver chloride}} \times 100$$

$$\frac{\text{Wt of chlorine found}}{\text{Wt of silver chloride}} \times 100$$

Compare the results of the two measurements and interpret (?)

\* See footnote, p. 12

Before cleaning the dishes, transfer the silver chloride to the bottle for silver waste

b Clean and dry two evaporating dishes, taking care to remove paper labels which may be pasted upon them Weigh each dish [Quant, balance], and record the results as shown below Place in each some sodium-hydrogen carbonate, in the one about 1 g and in the other about 2 g, and weigh again Treat both alike, as follows Dissolve the solid in pure dilute hydrochloric acid [R 52], adding little by little and covering with a watch-glass between successive additions to avoid loss by spitting When the solid has wholly dissolved, wash the watch-glass over the dish, and evaporate [Hood] the contents of the latter on the water bath, or on a beaker of boiling water (Fig 7) (Avoid loss of time by borrowing a second Bunsen burner and gas tubing temporarily from the storeroom) Allow the dishes to become perfectly cold, and weigh To make sure that the drying was complete, heat once more for half an hour and, when cold, weigh again This precaution is taken in all experiments of this kind The product is common salt

Dish No 1    Dish No 2

Wt of dish + sod bicarb

Wt of dish (empty)

Wt of sod bicarb

Wt of dish + salt

Wt of dish (empty)

Wt of salt

Ratio ( $\tau$ )

Calculate the proportion of carbonate taken to salt produced thus

Wt of carbonate    Wt of salt    1     $\tau$

Compare the two values of  $\tau$  found from the two differing quantities of the carbonate and interpret

What physical property of hydrochloric acid permits use of an excess of the acid without damage to the result? What form of statement of the law is verified directly by this experiment?

## CHAPTER III

### OXYGEN

**11 Sources** (p 12, footnote) Heat small quantities ~~of~~ barium peroxide, lead dioxide, potassium nitrate, silicon dioxide (sand), and manganese dioxide (dry this before use by heating it for a few minutes in a porcelain crucible) separately in a hard glass test-tube [Note 27] Observe whether any gas is given off, and apply the test of the glowing splinter of wood [Note 28] If the Bunsen flame gives no result, try the blast-lamp Note any changes in appearance during the heating and describe the residues [Note 29] Clean the test-tube carefully with hot nitric acid [CARE] and dry it [Note 26, p 12] after each experiment

*Note 27* — Use the clamp and ring-stand to support the tube, or grasp it by means of a strip of folded filter paper (Fig 8) In either case it must be kept in a horizontal position, otherwise condensed moisture may run down and cause it to crack



*Note 28* — Use a long splinter of pine wood bearing a spark at one end (why not an ordinary match?) Such a splinter is at once kindled by oxygen

*Note 29* — Beginning with this chapter include in your notes **equations** for all the chemical changes you observe When no change is observed, do not attempt to give an equation until otherwise instructed (Chap IX) In the present experiments the formulae of the materials used will have to be sought in the text-book The formulae of the products will also be sought in the book after the physical properties of the product and the evolution or non-evolution of oxygen have been noted and an indication of what to seek for has thus been obtained For other information in regard to the note-book, see the "General Directions," Notes 1-5, p 1

### 12 Catalytic Action

*a* Place in a test-tube a little potassium chlorate, fix the tube in a vertical position by means of a burette clamp attached to the ring-stand, and melt the substance at the lowest temperature at which this is possible (patience!) Note whether there is evidence of the evolution of oxygen. Now throw into the molten material a pinch of powdered manganese dioxide (?)

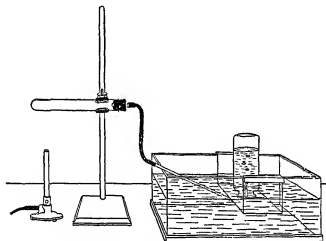


Fig 9

[Note 2, p 1], keeping the face out of the path of anything which may accidentally be projected from the tube. Interpret [R 27, 29] (?)

*b* Devise a way of showing that the manganese dioxide, used as in *a*, remains unchanged after the action, and that it is the potassium chlorate that loses its oxygen, and try it (?) Consult the instructor in regard to the details of your plan before executing it.

**13 Preparation** Mix on paper about 5 g of potassium chlorate and 2 g of powdered, dried (see 11) manganese dioxide

Place the mixture in a hard glass test-tube provided with a one-hole cork or rubber stopper and delivery tube (Fig 9, the deeply shaded parts are rubber) Test the apparatus to see that it is air-tight [Note 30, below]

Clamp the test-tube on the ring-stand and heat carefully, with a small flame, so as not to cause too violent an evolution of oxygen Collect four bottles of the gas over water in a pneumatic trough, taking care to remove the delivery tube from the water as soon as the bottles are full of oxygen (why?) The test-tube may be cleaned by allowing it to soak in water

*Note 30* — To test for air-tightness, place the end of the delivery tube in the mouth, withdraw some of the air by suction, and note whether or not the tongue will adhere to the end of the tube If it will not, there is a leakage which must be remedied

#### 14 Properties [Note 5, p 1]

*a* Place a very small amount of sulphur in a deflagrating spoon, ignite it, note the odor, and then lower into a bottle of oxygen (?) [Note 2, p 1]

Remove the spoon, and note the odor of the gas in the bottle Then add a little water to the bottle, close the mouth with the hand and shake (?) Test the water with blue litmus paper or solution [R 53, 258] (?) Make lists of such physical [R 19] and chemical properties of the product as you have observed (?)

*b* Place a little red phosphorus in the spoon, ignite it, and lower into the second bottle (?)

Proceed as in *a* Test with blue litmus [R 53] (?) Why does the product form a smoke, instead of remaining in the spoon?

(If yellow phosphorus is used, it must always be cut under water and handled with forceps Great care must be taken not to touch it with the hand, as it catches fire easily, and causes very severe burns Red phosphorus is safer, and should be employed if available)

*c* Lower a splinter of glowing charcoal into the third bottle,



holding it in the tongs or wrapping the end of a piece of copper wire round it (?)

Proceed as in *a* (use no litmus), and cover the mouth of the bottle with a glass plate. Add some limewater (calcium hydroxide) and shake again [R 384] (?)

**15 Slow Oxidation of Metals** Devise a way of showing that an loses a part of its substance (not, *eg*, that the iron gets heavier, but that the air diminishes in amount) when moist iron powder rusts, and try it. Submit your arrangement to the instructor for criticism before using it.

## CHAPTER IV

### HYDROGEN

#### 16 Interaction of Metals and Acids

a Place a few small pieces of each of the metals, tin (granulated), copper, iron (filings), zinc (gran), lead (gran), aluminium (turnings), and magnesium (wire) in separate test-tubes. Place in the measuring cylinder 20 c.c. of pure concentrated hydrochloric acid [R 52] and add an equal volume of water. Add 5 c.c. of the mixture to the contents of each test-tube (?). Observe each case critically [Note 31, below] and record the results [Note 29, p. 16], noting the order of the metals in respect to activity. Action on the aluminium will not occur until the tarnish has been removed from the surface by the acid. If no action occurs in the cold, try the effect of gentle heating. If heating seems to produce gas, remember that it may be hydrogen chloride (why?) or steam and not hydrogen. The presence of hydrogen may be inferred from continued effervescence (liberation of a gas in bubbles) when heat is not being furnished, and may be proved by the slight explosion which follows when a light is brought to the mouth of the tube. But hydrogen will not burn when mixed with much air or with other vaporous substances (why?). After the action has ceased, filter any one of the solutions and evaporate [Hoon] it to dryness on the sand bath (?).

Can you give any grounds for the belief that the hydrogen comes from the acid and not from the metal or the water?

Which metals, not used above, will displace hydrogen from dilute acids [R 60, and Appendix VII]? In what ways, if at

all, does the order of activity you have observed differ from that accepted by chemists?

In making the equations for these actions all that is needed, beyond the information given above and acquired by observation, is to find the formulæ of the products. These are not here to be sought by measurement, but in the text-book [R]

*b* Ascertain the influence of the physical state of the metal on its apparent activity by adding some zinc dust to the same acid [R 35, foot]

*c* Place one small piece of *pure* zinc into each of two test-tubes and add diluted sulphuric acid to both tubes. If little or no action takes place in the cold, try upon one tube the effect of heating (?). Try the effect of putting a platinum wire in contact with the zinc in the second tube (?). Notice where the hydrogen appears to come from, and explain [R 55]. Withdraw the platinum wire, add two drops of cupric sulphate solution and shake until the blue color is removed from the solution (?). Is the zinc still silvery? What is the substance upon the zinc [R 259], and what effect does it produce upon the apparent activity of this metal? Explain (?)

*d* Now compare (?) the behavior of concentrated sulphuric acid with that of the diluted acid used in 16 *c*, by placing some zinc (gran) in a test-tube and adding enough of the concentrated acid to barely cover the metal (?). After noticing the effect in the cold (?), apply heat (?). Odor (?). What products are formed [Note 31, below]?

*e* Try the interaction of acetic acid with zinc (gran) or iron (filings). Apply heat, if necessary.

\* *Note 31* — In observing an interaction a chemist first mixes the substances thoroughly by shaking. If nothing occurs, he then heats. If his eye detects evidence of the production of a gas or vapor, he finally smells the contents of the tube. Apply these three methods of observation to *d* before drawing any conclusion.

### 17 Other Methods of Obtaining Hydrogen

a Describe the result of throwing pieces of sodium and of potassium into water, as you recall having seen it [Class-room] Write the equations for these two actions (?) What other metals displace hydrogen from water [R 60]?

b Fit a test-tube with a one-hole cork and delivery tube (Fig 9) Pulverize about 2 g of sodium hydroxide, mix it intimately in the mortar with about 3 g of zinc dust, and place the mixture in the test-tube Insert the cork and delivery tube, test the apparatus for air-tightness [Note 30, p 18], and clamp the tube in a horizontal position (why?) Heat the mixture and collect the gas (?) over water (Fig 9) in a test-tube If the tube should crack [CAUTION!] cease heating at once To learn whether the gas is combustible, when the test-tube is full of the gas, close the mouth with the thumb and carry the tube, mouth downward, to a flame (?)

18 Preparation of Hydrogen [Same apparatus is used for 19 and 20] Fit a 250 c c flask, or w-m bottle, with a safety tube and ext tube (Fig 10), and test for air-tightness Place in the flask some commercial, granulated zinc, close the apparatus,

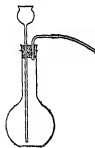


Fig 10

and attach to the L-shaped ext tube, by means of a short piece of rubber tubing, a longer glass delivery tube Now pour 30-40 c c of dilute hydrochloric acid through the safety tube Test the issuing gas until it is found free from air [Instructions The gas must not be ignited at once or the apparatus will be blown up (whence comes the air mixed with the hydrogen?) Collect samples of the gas from time to time by raising the delivery tube and inserting it to the upper part

(why?) of a small test-tube held in an inverted position Close the mouth of the test-tube with the thumb, and bring the mouth of the tube (still inverted) to a distant flame When the gas

contained in the test-tube, after the first explosion of the part nearest to the mouth, burns quietly, the gas is free from air. Call an instructor to inspect the test.] Keep the apparatus in operation for use in 19 and 20.

### 19 Properties of Hydrogen

a By collection over water in the pneumatic trough, fill a test-tube with hydrogen. Using this, and a similar test-tube filled with air, show by an experiment that hydrogen is lighter than air (?).

Fill another test-tube with hydrogen and apply it closely, mouth downward, to a test-tube of air, mouth upward. Allow the tubes to remain in this position for three minutes, then bring first the lower and then the upper tube quickly to a flame (?). What fact about diffusion does the result illustrate?

b Fill another test-tube with hydrogen, as in a, and, holding it mouth downward, insert into the tube a burning splinter. Does the splinter continue to burn? Explain.

c Remove the glass delivery tube, and connect a glass nozzle with the exit tube of the generating flask. Press the mouth of the nozzle close against the side of a cold, dry beaker. If moisture is deposited from the unlighted gas (what is its source?), fill a U-tube with calcium chloride [R 475] and connect it between the exit tube and the nozzle. Does the gas now deposit moisture upon a beaker? If not, ascertain that the issuing gas is not explosive (see test in 18), and set fire to it. What is the color of the flame? Does the color change, and, if so, why? Hold a cold, dry, inverted beaker over the flame. What is deposited on the beaker? Why did we use dried hydrogen for this experiment? Keep the apparatus in operation for 20, unless a Kipp's apparatus is available or hydrogen is furnished in the laboratory.

Turn off the gas supplying the Bunsen burner, remove the burner, and push a glass nozzle tightly into the end of the gas tubing. Turn on a gentle stream of gas and set fire to it. Hold

a cold, dry beaker over this flame (?) What inference in regard to illuminating-gas do you draw?

**20 Reduction by Means of Hydrogen** [Two students working together] Fit a hard glass tube, 25-30 cm long and open at both ends, with perforated corks and short glass tubes (Fig 11) Support it on the ring-stand by means of a clamp grasping

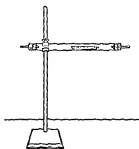


Fig 11

it close to one end Dry 1-2 g of ferric oxide by heating in a porcelain crucible Put the oxide into the porcelain boat and place the latter in the hard glass tube near the end remote from the clamp (why?), but not so near that the subsequent heating will char the cork Insert the corks with their tubes Connect the tube nearest to the boat with a Kipp's apparatus and drying bottle (Fig 23,

p 89) delivering dry hydrogen, or with the laboratory supply of the gas, or with the apparatus furnishing dry hydrogen used in 18

Test the issuing gas to see that it is not explosive (see 18) and repeat the test every time the apparatus is opened Now heat the boat and contents, at first gently by waving the flame under the tube, and later strongly until the material is red-hot Observe the effect upon the ferric oxide [R 635] (?) Does anything condense in the cooler end of the tube?

What is the action of steam upon heated iron [R 51-52]?

Repeat the above experiment, using freshly heated aluminum oxide in place of ferric oxide, and otherwise following the directions exactly (?) If no effect is noticed after an oxide has been at a red heat for three minutes, absence of action may be inferred How do you account for the result obtained with aluminum oxide? Which oxides are reducible by hydrogen [R 60]?

## CHAPTER V

### COMPOSITIONS AND FORMULÆ OF SUBSTANCES

21 **Composition of a Sulphide of a Metal** [Quant Note 22, p 8] Weigh the crucible (without cover) to the nearest centigram, counting the weights as described in 5. Place about 2 g of "reduced" nickel (do not attempt to take this amount, exactly) in the crucible and weigh again. Set down the weighing as shown below. Put about 2 g of sulphur in the crucible and set the latter on the pipestem triangle (Fig 12). Set the cover on the crucible, and heat gently so long as sulphur vapor burns [Hood] at the chink between the crucible and cover. Heat strongly for 1-2 minutes. Then hold the flame against the upper portion of the crucible, so that all free sulphur may be driven off. When the crucible is cold (not before), remove the cover and weigh.

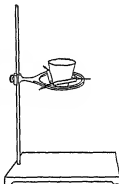


Fig 12

Wt of crucible + nickel	g
Wt of crucible, empty	<u>g</u>
<b>Wt of nickel taken</b>	<u><u>g</u></u>
Wt of crucible + nickel sulphide	g
Wt of crucible + nickel	<u>g</u>
<b>Wt of sulphur combined</b>	<u><u>g</u></u>
Wt of crucible + nickel sulphide	g
Wt of crucible, empty	<u>g</u>
<b>Wt of nickel sulphide</b>	<u><u>g</u></u>

Calculate the percentage composition of nickel sulphide (?) From your results, calculate the formula of nickel sulphide [R 45] and show in your notes the method of calculation (?) Make the equation for the union of nickel and sulphur

**22 Composition of an Oxide of a Metal** [Quant Note 22, p 8] On account of the difficulties attending the making, the collecting, or the weighing of most oxides formed by direct union, the following indirect method is suggested. It consists in converting a known weight of a metal into the nitrate of the metal by the action of nitric acid, and obtaining the oxide by decomposition of this salt. Make no equations for these actions.

*a* Composition of an oxide of iron. Weigh an evaporating-dish of medium size, place in it about 1 g. of pure iron wire, and weigh again. Count the weights as described in 5, and record the results as shown below (?). Cover the dish with a watch-glass, convex side downward, and add 10 c. c. of pure dilute nitric acid. Set the dish, covered, on the water bath until the iron has dissolved, adding a few drops of concentrated nitric acid if any of the wire remains unattacked [Instructions]. Then rinse the cover-glass carefully into the dish and remove it, and evaporate the solution to dryness on the water bath or on a beaker of boiling water [Hood]. When the residue (what is it?) is dry, place the dish on a clay triangle supported on the ring-stand and heat carefully with a burner held in the hand as long as any red fumes are given off. During this process, and especially at first, great care and patience must be exercised, as too rapid heating may cause solid particles of the product to be thrown from the vessel. If any crackling noise is observed, remove the burner at once. When, after final strong heating of every part of the material, red fumes or other evidence of continued change can no longer be perceived, allow the dish and contents (?) to cool and weigh them. To make sure that the decomposition was complete, heat once more, cool, and



weigh again. This precaution is always necessary in experiments of this nature.

Before cleaning out the dish, show the results of the calculation (below) to an instructor. If the percentage of oxygen is too low, and no loss from spitting occurred, some iron may have remained unattacked. To remedy this, moisten with concentrated nitric acid, heat once more, and weigh (?).

Wt. of crucible + non	g
Wt. of crucible, empty	<u>g</u>
Wt. of iron	<u>g</u>
Wt. of crucible + oxide of iron	g
Wt. of crucible + non	<u>g</u>
Wt. of oxygen	<u>g</u>
Wt. of crucible + oxide of non	g
Wt. of crucible, empty	<u>g</u>
Wt. of oxide of iron	<u>g</u>

Calculate from your results the percentage composition of the oxide of iron (?).

Assuming the atomic weights of iron and of oxygen to be 55.8 and 16, respectively, calculate from your data the formula of the oxide of iron [R. 45]. What is the name of this oxide? What other oxides of iron are known [R]? What is the valence of the iron in this oxide?

b. Pure zinc (about 1 g.) may be used instead of iron. The manipulation is the same as in 22 a. The residue from evaporation is a syrup-like body, however, which cannot be dried. Extra caution must, therefore, be used in heating this to avoid loss by spitting.

Tabulate the results as shown in 22 a, and make the corresponding calculations (?).

c. Magnesium (about 1 g.) may be used instead of zinc (22 b). Equal care is required during the evaporation and heating. Tin (about 1 g.) may also be used.

**23 Composition of a Chloride** [Quant. Note 22, p. 8] Weigh an evaporating-dish of medium size, place in it about 2 g. of pure zinc, and weigh again (?). Tabulate the results as shown below. Add a little diluted (1 Aq. 2 acid), pure, concentrated hydrochloric acid and cover with a watch-glass, convex side downward. If the action is very slow, the tip of a platinum wire may be placed in contact with the zinc. Maintain a brisk action by further additions of concentrated hydrochloric acid in very small amounts at a time. Final excess of the acid should be avoided, as time will be lost in the subsequent evaporation. When the metal is completely dissolved, rinse the cover-glass and platinum wire carefully into the porcelain dish and remove them. Allow the solution to evaporate as far as possible on the water bath or on a beaker of boiling water [Hood]. Now place the dish on the ring-stand, and, using a small Bunsen flame, allow the syrup-like solution to evaporate slowly to dryness. Then heat the white mass to the point at which it has completely melted and no further. The best way to achieve this with the minimum rise in temperature is to let the Bunsen flame play on the surface from above. Overheating must be avoided, because the product is volatile, giving white fumes, at high temperatures. The moment the dish has so far cooled that the hand can be borne upon the bottom, wipe the dish carefully and weigh it. The substance absorbs moisture greedily from the atmosphere, hence expedition is required in cooling and weighing if accurate results are to be obtained. To insure accuracy, the melting, cooling, and weighing should be repeated, and the lower result taken as correct.

Wt. of dish + zinc	g
Wt. of dish, empty	<u>g</u>
Wt. of zinc	<u><u>g</u></u>
Wt. of dish + zinc chloride	g
Wt. of dish + zinc	<u>g</u>
Wt. of chlorine	<u><u>g</u></u>

From your results, calculate the equivalent weight of zinc, i.e. the weight combining with 35.46 parts of chlorine (?)

Assuming the atomic weights of zinc (65.37) and of chlorine (35.46), calculate from your results the formula of zinc chloride.

Express the whole action of hydrochloric acid on zinc in symbols by making the equation in accordance with these conclusions. Which of the factors in the equation have you determined experimentally, and which not? What law do we use in assuming that the undetermined factors are correct?

What weight of 35 per cent hydrochloric acid was actually required for the weight of zinc taken? About how much did you use?

#### 24 Combining Weights of Lead or Silver and Chlorine

From the weights of lead (9) or silver (10 a) and chlorine found to combine, calculate the formula of lead (or silver) chloride.

#### 25 Equivalent Weight of a Metal by Displacing Hydrogen [Quant]

a First fill the pneumatic trough and 1-liter bottle with water so that the liquid may acquire the temperature of the room. Fit a 100 c.c. flask somewhat as in Fig. 10, using in place of the thistle-tube a dropping-funnel (see 25 b). To carry a doubly-bored cork the mouth of the flask must be rather wide. A larger flask than 100 c.c. must not be employed on account of the waste of acid its use would entail. A sufficiently wide test-tube, or a w.-m., 90 c.c. bottle, however may be used. The stem of the dropping-funnel must reach to the bottom of the flask (or test-tube or bottle), and the inner end of the L-tube must not project below the bottom of the cork. Attach a rubber or glass delivery tube and see that the apparatus is air-tight. Weigh a piece of chemically pure zinc, taking about 2 g. (?) Without detaching your platinum wire from the glass rod, wrap it tightly round the zinc (why?) and allow the whole to slide gently into the flask. Fill the apparatus completely, from the

top of the stem of the funnel to the tip of the delivery tube, with water. Close the stopcock when the bulb has almost emptied itself. Invert the 1-liter bottle, filled with water, on the shelf of the pneumatic trough, and put the delivery tube in position.

Fill the globe of the funnel with pure concentrated hydrochloric acid and admit this to the flask, a little at a time, in such a way that a steady, but not too violent, action takes place. A good deal will be needed at first before sufficiently rapid action begins (why?). When the metal is entirely dissolved, drive all the gas over into the bottle by pouring water once more through the funnel (be careful that no air is carried over with the water).

The weight of the hydrogen which has been displaced by the weighed quantity of zinc is to be ascertained in this experiment, not by direct weighing, but, as follows, by measuring the volume of the gas and calculating its weight from this and the density of hydrogen.

When the gas has acquired the temperature of the water and room, lower the bottle until the level of the water outside and inside is the same. If there is still a good deal of water in the bottle, the latter may have to be inclined to accomplish this and the following operation. Close the bottle with a cork while it is in this position and remove it from the trough. To find the volume of the gas, measure with the graduated cylinder the volume of water required to completely fill the bottle (?). The volume of water needed is equal to the number of c.c. of hydrogen. Record the temperature of the hydrogen by reading a thermometer hung in the laboratory close to the apparatus. Read the barometer, and record the corrected reading [R 71] (Appendix I). Since the hydrogen is mixed with water vapor, correct for the latter by subtracting the aqueous tension (Appendix II) at the observed laboratory temperature from the corrected barometric reading. This gives the true partial pressure of the hydrogen.

<b>Wt of zinc taken</b>	<b>g</b>
Vol of hydrogen obtained	c c
Temperature	°
Barometric height (corr)	mm
Tension of aqueous vapor	mm
Press of hydrogen, corr	mm
Vol of hydrogen at 0° and 760 mm	c c
<b>Weight of this hydrogen</b>	<b>g</b>

Reduce the volume of the hydrogen, by rule, from the observed temperature and partial pressure to 0° and 760 mm [R 72] Find by calculation (1 liter weighs 0.09 g at 0° and 760 mm) the weight of the hydrogen obtained Calculate the equivalent weight of zinc,  $z$ , the weight of the metal ( $\tau$ ) which displaces 1.008 g of hydrogen

$$\text{Wt of hyd} \quad \text{Wt of zinc} \quad 1.008 \quad \tau$$

Calculate from the result how many equivalent weights of hydrogen would be displaced by 65.4 g, the gram-atomic weight, of zinc What is the valence of zinc? How many formula-weights of hydrogen chloride are required to furnish the hydrogen displaceable by one atomic weight of zinc? Write the left-hand side of the equation in accordance with this result

Wash the trough carefully until it is absolutely free from acid, and put it away in an inverted position to avoid rusting

b The above experiment may be performed with magnesium (about 0.9 g), iron (about 1.8 g), or aluminium (about 0.8 g) in place of zinc

In the absence of a dropping-funnel, a substitute may be made by connecting a funnel with a straight tube by means of a rubber joint closed with a pinch clamp (Fig 13) Or, the aspirator (Fig 14) may be used here, the metal (half the above quantities), water, and a smaller

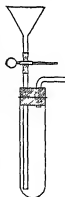


Fig 13

tube containing the acid being placed in the test-tube, and the mixing being effected by inclining the bottle after the apparatus is connected

**26 Inter-Equivalence of Equivalent Weights** (Law of Reciprocal Proportions) If **22 b** was performed, compare the quantity of zinc which combined with 8 g of oxygen with that which in **25 a** was found to displace 1.008 g of hydrogen. If they are identical, these two quantities of oxygen and hydrogen are chemically equivalent and may combine with one another. What substance has precisely this composition?

If magnesium was used, in **25 b**, compare the quantity with that combining, in **22 c**, with 8 g of oxygen and answer the same question.

## CHAPTER VI

### WATER.

**27 Purity of Water** Place a few drops of distilled water on a clean watch-glass (not an evaporating-dish Why?) and evaporate on the water bath. Do the same with ordinary water. Observe whether any stains remain on the glasses (?). What class of impurities would leave no trace of their presence in this test?

**28 Union with Oxides** Place a pinch of cupric oxide in a test-tube and wash it by shaking with a little distilled water and pouring off the liquid. Add more water and shake again. Test this latter solution with litmus paper (?). At the same time test a sample of the water with litmus paper and compare the tints. Repeat with barium oxide (?).

Recall the behavior of acid-forming oxides examined in 14. Some oxides do not interact readily with water (which?). These oxides which do interact may be divided, according to the natures of the products they give, into two classes. What are those classes, and which oxides belong to each? What are the two classes of elements whose oxides belong to the two groups, respectively [R 94]?

### **29 Hydrates**

a Heat some blue vitriol (p 4, footnote) gently in a porcelain crucible (?). Allow a very small portion of the white powder to stand exposed to the air on a watch-glass (?). Dissolve the remainder by boiling with the minimum amount of water required to dissolve it, and set the solution aside (?). What chemical actions have taken place in these three operations?

b [Quant] Place small quantities (about 1 g.) of Glauber's salt and of blue vitriol in two porcelain dishes and ascertain the gross weight in each case. Allow the dishes and contents to remain for 24 hours or more and weigh again (?) Interpret the results [R 96]

c Pulverize small quantities of barium chloride, potassium nitrate, magnesium sulphate, and potassium dichromate separately in the mortar. Warm them, separately, in dry test-tubes and notice whether they undergo any change [R]. Mere melting does not show that the substance is a hydrate.

Are all crystalline substances hydrates? Classify the substances you have examined into two groups with reference to this property.

d Take in a test-tube about 5 c.c. of commercial, concentrated sulphuric acid, place in it a crystal of blue vitriol and let the materials stand for an hour, or more (?) [R 286]. Now heat the contents of the tube to the boiling-point of the acid [Hoop], holding the test-tube in a test-tube holder, keeping it far from the clothing, and taking care that none of the contents spurt out upon the hands or face [CAUTION. Sulphuric acid burns are very painful. Note 16, p. 2]. After the contents of the tube have settled, pour off the clear liquid into another tube. On the following day, examine the little, shining particles on the sides of the tube. What is their color, and condition? Of what are they composed [R 509]?

Are the compounds (such as cupric sulphate) which, in presence of water, yield crystalline hydrates, amorphous or crystalline in its absence? What is the true significance of the crystalline condition [R 97]?

e Take a clean match and, after dipping it in a solution of cobalt chloride, write upon a piece of white paper. After the writing is dry, warm the paper gently by waving it above a Bunsen flame (?) Now, breathe repeatedly upon the writing (?). Write equations for the actions that have occurred [R 639].



**30 Formula of a Hydrate** [Quant] Put about 1 g of crystals of gypsum in a weighed porcelain crucible and weigh again. Place the crucible on the clay triangle, place the lid so as partly to cover the crucible, and heat to redness until no further loss in weight occurs. Determine by difference the loss in weight (water) and the weight of the calcium sulphate remaining.

The formula of gypsum must be  $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ . Assuming the formula-weights of calcium sulphate ( $\text{CaSO}_4 = 136$ ) and of water ( $\text{H}_2\text{O} = 18$ ) calculate from your data the value of  $x$ .

Wt of calcium sulphate    Wt of water     $136 \quad x \times 18$

What is the formula of gypsum?

## CHAPTER VII

### MOLECULAR AND ATOMIC WEIGHTS

#### 31 Molecular Weight of Oxygen [Quant]

*a* Powder some potassium chlorate, and dry it on a watch-glass on the radiator, or high above a small Bunsen flame, or in a drying oven. Construct an aspirator (Fig 14), using the 1-liter bottle, and connect it with a hard glass test-tube. Fit a nozzle to the rubber tube and slip a pinch clamp over the outlet tube (syphon) in readiness for closing, at a later stage, the

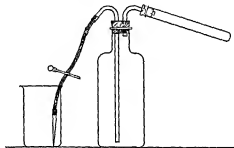


Fig 14

rubber tube that connects the two glass tubes. Having inserted the stopper tightly and connected the test-tube, test the apparatus to see that all the joints are air-tight [Instructions: Place some water in the bottle, blow a few bubbles of air into the apparatus through the syphon, and observe whether the water remains permanently elevated in the vertical tube. Absolute certainty that the apparatus is air-tight must be reached before proceeding further.]

Carefully weigh the hard glass test-tube, then place in it between 1 g and 2 g of potassium chlorate and weigh again. Record the results as shown below. More than 2 g is not needed, less than 1 g will not be sufficient. Subtraction gives the exact weight that has been employed. Fill the bottle almost, but not quite, to the shoulder (not the neck) with tap water. After reattaching the test-tube, make sure that the apparatus is once more air-tight, by repeating the above-described test. Next fill the syphon and nozzle completely with water by blowing sharply through the latter, and close the clamp. Allow the nozzle to touch the bottom of a beaker (400 c c) containing some water. Now open the clamp and raise the beaker till the levels of the water in this and the bottle are the same, and the gaseous pressure therefore alike in both. Close the clamp again, empty the beaker and replace it in position.

Wt of tube with chlorate	g
Wt of tube with residue	<u>g</u>
Wt of oxygen	<u>g</u>
Vol of water driven over	cc
Temp in lab	°
Temp near barometer	°
Barometric height	mm
Correction	<u>mm</u>
Barometer (corr)	mm
Aqueous tension at temp of lab	<u>mm</u>
Partial press of ox	<u>mm</u>

Open the clamp once more and decompose the compound very slowly by heating, catching in the beaker the water driven over by the gas. At least 250 c c of water should be driven over. During the earlier stages a smoke, consisting of solid particles, will arise. This must on no account be driven into the connecting tube, as all the solid must remain in the test-tube to be weighed (why?) Suspend the heating as often as may be necessary to let this smoke settle. During such inter-

vals of waiting see that the nozzle is constantly immersed in the water that has already passed over (why?) Stop heating if the tube shows signs of softening [Note 32, below] or when the decomposition is complete. For the purpose of this experiment (see 31 b) it is not necessary that the action should be carried to completion. If, when the heating is stopped, the nozzle is not under water, raise the beaker until it is well covered. Allow the whole apparatus to stand until it has reached the temperature of the air. Some water will return to the bottle by the syphon during the cooling. As this transference of water is essential to the success of the experiment, at no stage should air be allowed to enter the syphon through the nozzle. Equalize the levels of the water in both vessels by raising or lowering the beaker, and then close the clamp.

Measure the volume of water in the beaker by means of the graduated cylinder (?). This represents the number of c c of water displaced, and hence of oxygen evolved in the operation (what of the air originally in the apparatus?) Weigh the test-tube once more with care [Balance] (?). Observe at the same time the temperature in the laboratory to learn the temperature of the oxygen (?), and read the barometer [Note 33, below] to learn the pressure of the air and therefore of the oxygen (?).

Subtract the aqueous tension (Appendix II) [R 72] at the observed laboratory temperature from the barometric reading (corr.) to get the true (partial) pressure of oxygen in the bottle. Reduce the volume by rule to 0° and 760 mm [R 71-72]. The weight of this volume of oxygen is obtained by subtracting the weight of the test-tube and residue from the weight of the test-tube and potassium chlorate originally taken. Calculate by proportion from the data obtained the weight of 1 liter of oxygen ( $x$ ).

Vol of ox found    Wt of ox found    1000 c c

Calculate also the weight of 22.4 liters (?) To what class of

gases would the use of the aspirator be confined for purposes like the above?

*Note 32* — To avoid softening of the glass, through overheating, watch the color of the Bunsen flame. The blue flame is tinged with a yellow color (caused by compounds of sodium in the glass) where the flame encounters the overheated part of the tube.

*Note 33* — When the barometer is read, the height must be "corrected" to that of a column of mercury at  $0^{\circ}$  (**Appendix I**)

*b* Detach the hard glass test-tube from **31 a** and drive off the last traces of oxygen by heating strongly every portion of the tube to which any of the residue adheres. Allow it to cool and weigh. Record the result, as shown below. Obtain the weight both of the residue (potassium chloride) and of the total oxygen, by difference.

Wt of tube with chlorate

Wt of tube with chloride

Wt of oxygen

Wt of tube with chloride

Wt of tube empty

Wt of chloride

Assuming the formula of the chloride to be  $KCl$ , that of the chlorate is  $KClO_3$ . The formula weight of  $KCl$  being  $39.1 + 35.46 = 74.56$ , find the formula weight of  $O_2$  by the proportion

Wt of  $KCl$  found    Wt of oxygen found    74.56     $y$ ,

where  $y = O_2$ . This will be a multiple of 16 by a whole number (why?), if the measurement has been carried out successfully. What formula do you find for potassium chlorate? Write the equation for the decomposition of the chlorate.

**32 Law of Multiple Proportions [Quant]** If the quantitative decomposition of potassium chlorate (**31 b**) was carried out, dried potassium perchlorate may be decomposed in the same way and the results compared. Weigh an open, long, hard glass test-tube. Place in it about 1 g. of potassium perchlorate

and weigh again. Then heat the tube and drive off the oxygen slowly, and weigh again. Heat strongly once more, to constant weight. Ascertain by difference the weights of potassium chloride (residue) and of oxygen.

The formula of the perchlorate is  $\text{KClO}_x$ . Calculate from your data how much oxygen ( $\text{O}_x$ ) is combined with 74.56 g., the formula-weight of potassium chloride,  $\text{KCl}$ . This result, the formula-weight of the oxygen, will be a multiple of 16. Compare this formula-weight of oxygen with that found in the experiment with potassium chlorate, and show how the results illustrate the law of multiple proportions. Find the formula of potassium perchlorate and write the equation for the decomposition of the compound.

### 33 Molecular Weight of an Insoluble Gas [Quant]

a Fit a round-bottomed 300 c.c. flask [Store-room] with a rubber stopper through which passes a short glass tube. To the latter attach a short rubber tube with an open screw clip [Store-room]. Place 40 to 50 c.c. of water in the flask, boil the water vigorously for about ten minutes to expel the air from the flask. Lower the flame, close the clip, and then *at once* remove the flame.

Wt. of flask and water + air	g
Wt. of flask and water	<u>g</u>
Wt. of air	<u><u>g</u></u>
Vol. of flask (total)	c.c.
Vol. of water (remaining)	<u>c.c.</u>
Vol. of air	<u><u>c.c.</u></u>
Barometric height (corr.)	mm
Tension of aqueous vapor	<u>mm</u>
Pressure of air, corrected	<u><u>mm</u></u>
Temperature	°

Wipe the flask, and weigh it when cold (?). Open the clip slowly to admit air, and weigh again (?). Record the weights (see above). The increase is the weight of the air which

entered To learn its volume, measure in the graduated cylinder the volume of the water remaining (?), and then the total volume required to fill the flask to the bottom of the stopper (?) Record also the temperature (?) and barometric pressure (corr) (?) and subtract from the latter the tension of the aqueous vapor in the flask (Appendix II)

Reduce the volume of the air from the observed temperature and barometric pressure (as corrected), to  $0^{\circ}$  and 760 mm [R 72]

From the weight of the air, and its volume at S T P, calculate the density (wt of 1 cc) of the air (?), and also weights of 1 liter (?), and of 22.4 liters (?)

b By admitting other gases, instead of air, this method may be used for measuring the densities of gases which are insoluble in water Name several gases to which this method could be applied (?)

By calculating from the results the weights of 22.4 liters, the molecular weights of such gases are obtained

**34 Dulong and Petit's Law** According to Dulong and Petit [R 108], if the correct atomic weight, when it has been found, is multiplied by the specific heat of the element in the solid form, the product is a number which in most cases lies between 6 and 6.8

Take the values of such equivalent weights as you have found experimentally, viz, zinc (23), lead (24), silver (24), zinc (25 a), magnesium (25 b), iron (25 b), aluminium (25 b), and multiply each by the corresponding specific heat (Appendix III) If the result is about 6.4, the atomic weight is the same as the equivalent weight If not, multiply the equivalent weight by the smallest integer which will bring the final product within the limits 6 to 6.8 The integer used is the valence of the element, and the product of the equivalent weight and the valence is the atomic weight Show the working in your notes and give a list of the atomic weights and valences found

## 35 Calculations

a The weights of 1 G M V (22.4 liters at 0° and 760 mm) of several compounds of carbon are as follows

Substance	Wt 22.4 l	Wt carb	Wt hyd	Wt ox	Formula
Carbon monoxide	28.00	12		16	
Carbon dioxide	44.00	12		32	
Methane	16.032	12	4.032		
Ethylene	28.032	24	4.032		
Glycaine (vapor)	92.064	36	8.064	48	

What value should you select for the atomic weight of carbon? The atomic weight and symbols being hydrogen H = 1.008, oxygen O = 16, carbon C = ?, write the formula of each of the five compounds (?)

b The density (wt of 1 c.c. at 0° and 760 mm) of ethylene chloride is 0.00433 g. What is the molecular weight?

c Using the weights of 22.4 l., given above, find the weight of 1 c.c. (the densities) of methane and of carbon dioxide (?)

d How do the densities of the five substances compare with that of air?



## CHAPTER VIII

### SOLUTION

#### 36 Conditions for Rapid Solution

*a* Take two large crystals of cupric sulphate of equal size, and yet of such size that each can be slipped into a test-tube. Provide two dry test-tubes with corks to fit. Pulverize one of the crystals very finely in the mortar, so that no large particles are visible. Place the powder in one test-tube and the crystal in the other. Add from the graduated cylinder 20 c c of water to each. Cork the tubes quickly, note the time on a watch(?), and shake the tubes quickly and continuously. Note the time when the powder has all dissolved (?) and when the crystal also has dissolved (?). Compare the total times required for each? Account for the difference (?)

*b* Take again two nearly equal-sized, but smaller crystals of cupric sulphate. Fill two test-tubes with water. Put one of the crystals into one of the tubes. Drop the other crystal into the second tube (Fig 15), so that it is covered by the water, but rests on a narrow strip of ordinary paper. Note the time (?). Set both tubes upright in the rack. How long does each crystal take to dissolve? Account for the difference (?)

If you had to dissolve a large amount of material quickly, with the least expenditure of effort, how should you proceed (In answering, take the results of both *a* and *b* into account)?

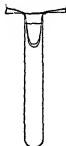


Fig 15

c On to a strip of paper dipping under water (Fig 15), drop a crystal of potassium permanganate (?) Explain (?)

### 37 Choice of Solvents

a Place 1 c c of powdered rosin in each of two dry test-tubes Add to one 5 c c of alcohol and to the other 5 c c of water and shake both (?)

Pour the alcoholic liquid into a large beaker full of water In what ways is a suspension like a solution (?) and how does it differ?

Should you remove rosin (or varnish or a similar gum) from clothing with water? With alcohol?

b Place a small piece of lard, half the size of a pea, in each of two test-tubes Add 2 c c of water to one and 2 c c of carbon tetrachloride \* (or carbon disulphide or ether) to the other and shake (?) How should you remove grease from clothing? (In removing a grease-spot, place the part flat on a piece of blotting paper, to absorb the solution, and rub the spot with a rag dipped in the solvent)

c Use small pieces of solid paraffin as in b, employing water and gasoline (petrol) or benzene as solvents

d Take 10 c c of water in each of three test-tubes To one add a single drop of alcohol and shake Does the alcohol dissolve? Add more alcohol, a few drops at a time, until about 5 c c have been added Has the amount added yet become greater than the water can dissolve?

To the second tube add carbon tetrachloride (or carbon disulphide) in the same way, and answer the same questions (?)

To the third add gasoline (or benzene) in the same way, and answer the same questions

If you had a mixture of sugar (which is soluble in water) with fat on a piece of cloth, how could you remove first one and then the other component of the mixture?

\* Non-inflammable Carbon disulphide or ether must not be used near a flame

**38 Degrees of Solubility**

a Place 1 c c of pulverized calcium sulphate in a test-tube and shake with 10 c c of water for 2-3 minutes. Filter the mixture, catching a few drops of the clear filtrate on a watch glass. Evaporate to dryness (?). Repeat with 1 c c of pulverized calcium carbonate (chalk), rejecting the water with which it is first shaken (?). Compare the deposits on the watch glasses (?). Which of these substances do you find to be more soluble? What are the amounts of these salts dissolved by 100 c c of water at 18° [R. Appendix IV]? In what ratio is calcium sulphate more soluble than calcium carbonate [R. Appendix IV]? In what ratio is calcium chloride more soluble than calcium sulphate [R]? Which of all these substances are spoken of as "insoluble"?

What conclusion should you have drawn from mere shaking with water, without completing the test?

Was the solution you evaporated saturated? Was it concentrated? What is a saturated solution?

b Take about 10 c c of water in a test-tube, add to it not more than 1 c c of lead nitrate solution, and mix. Now add about 2 c c of dilute hydrochloric acid (?). Repeat, heating the mixture to the boiling-point before adding the hydrochloric acid (?). Examine this tube again, after the contents have cooled (?). Interpret the result. Is lead chloride an "insoluble" substance [R. Appendix IV]?

c [Quant.] Reduce to a fine powder 10-15 g of potassium dichromate, using the larger amount in warm weather, the smaller in cool. Prepare a saturated solution of the substance by placing it in a flask with 50 c c of water and shaking at intervals for ten minutes. So much of the solid must be taken that an undissolved residue remains.

Take the final temperature of the solution. Now pour the clear solution into a burette attached to the ring-stand, filling the apparatus completely to the point of the nozzle with the

liquid (6*b*) Read the level of the lower side of the meniscus Weigh [Quant] a clean, dry evaporating-dish, run into it about 22-24 c c of the solution, and weigh [Quant] the dish and contents Read also the level of the meniscus and note the volume of solution used Now evaporate the weighed portion of the solution completely to dryness upon a water bath, or on a beaker of boiling water, and weigh again Determine by difference the weights of the dry dichromate here found, and of the water in which it was dissolved Calculate from the data the weight of dichromate which would be dissolved by 100 c c of water at the observed temperature (?)

From the volume of the part of the solution evaporated, and the weight of dichromate found in it, calculate also the molar solubility [R 125] of potassium dichromate at the observed temperature Compare the results with those which would be obtained with potassium chromate  $K_2CrO_4$  (Appendix IV) (?)

**39 Solution Gases in Liquids** Half fill a 1-liter bottle with distilled water, cork, and shake vigorously till the water is saturated with air Take the temperature of the water and also the barometric reading Fit a small flask (100 c c) with a one-hole cork and delivery tube (Fig 16) and measure its content



Fig 16

up to the lower surface of the cork Completely fill the whole apparatus, including the delivery tube, with the prepared water, and boil, collecting the gas in a small test-tube inverted over water When no more gas

comes over, equalize the levels of the water in the tube and trough (or beaker) and mark the level in the tube with a thin rubber ring (cut this from a piece of rubber tubing) Measure the volume which the air occupied Correct the volume for the aqueous vapor present only, obtaining thus the volume of the air when dry and at the observed temperature and pressure

Calculate the volume of air dissolved by 100 c c of water at the observed temperature and pressure (?) What proportion of its own volume of air has the water dissolved?

**40 Two Immiscible Solvents, Extraction** Place one small particle of iodine in each of three test-tubes and add to one water, to the second potassium iodide solution, to the third carbon disulphide, and shake each (?) If any iodine remains undissolved, pour off that solution into a clean test-tube. Now add a drop or two of carbon disulphide to the first two solutions, shake again (?), and describe carefully what seems to have happened. Deduce from this the relative solubility of iodine in the three solvents.

#### 41 Temperature and Solubility

*a* Take about 6 g of the dichromate and boil with 10 c c of water in a test-tube. How does the solubility differ from that found in 38 c? Allow the clear solution to cool (?) Explain the result. What sort of curve of solubility would this substance exhibit (Appendix V)? Draw a curve of this type in your notes (?)

Warm the contents of the tube carefully once more until all has dissolved. Then hold the tube in running water to cool it rapidly (?) Describe the contents (?) Note two differences (in size of particles and in color) between the results of slow and of rapid cooling and explain each (?)

*b* Take about 6 g of sodium chloride and boil with 10 c c of water in a test-tube. Pour the clear liquid immediately into another test-tube. Examine this when cool (?) Is salt much less soluble in cold than in boiling water? How would its curve of solubility differ from that of potassium dichromate? Draw a curve of this type in your notes (?)

**42 Supersaturated Solution** Heat some anhydrous sodium sulphate strongly in a porcelain dish and allow it to cool. Take about 10 c c of water in each of two test-tubes. To one portion add Glauber's salt, previously pulverized in a mortar,

until, after shaking, a considerable excess remains undissolved. Saturate the other portion with the cold anhydrous sodium sulphate in the same manner. Perform the last operation rapidly, taking care not to introduce any particles of the hydrate, and do not let the solution stand before use. Now decant the two liquids into clean test-tubes, disregarding the cloudiness of one of them. Then add a little of the anhydrous substance to the solution first made and a small crystal of Glauber's salt to the contents of the second test-tube and shake both (?). After a short time, examine the contents of each again (?). Interpret the results [R 132-133].

#### 43 Freezing-Points, Deliquescence, Boiling-Points

a If pulverized ice were to be added to water until the solid no longer melted, what would be the temperature of the mixture? If ice were to be added to the aqueous solution of some substance, until the ice no longer melted, how would the temperature differ from that of water and ice? Why does this difference exist [R 134]? Why does salt thrown upon ice cause the latter to melt?

b Place some dry potassium carbonate (or pulverized calcium chloride) in a small beaker or crucible. Set the vessel in an evaporating dish containing water, and invert over it a larger beaker so that the edge of the latter is under the liquid. Examine the material from day to day (?). Remembering that there is moisture upon the surface of even "dry" bodies, and that therefore a solution of potassium carbonate was present with the solid, explain the change [R 135]. To what class of substances do those which deliquesce all belong? Is deliquescence a physical or a chemical change?

c Fix a test-tube containing about 10 c.c. of water in a clamp upon the ring-stand. Suspend the thermometer from a ring by means of a thread, in such a way that the bulb is immersed in the water. Boil the water, using a small Bunsen flame, and read the temperature (?). Now add to the boiling water

about 2-3 g of dry calcium chloride and, after solution is complete, read the temperature of boiling again (?) Add another, equal portion of calcium chloride, boil, and repeat the temperature reading after the whole has dissolved (?) Explain [R 135]

#### 44 Properties of Solutions Volume Changes and Thermal Effects

*a* [Quant] Take about 25 g of potassium carbonate and determine its weight to the nearest tenth of a gram. Assuming the specific gravity of this substance to be 2, calculate the volume of the amount you have taken (?) Place in the graduated cylinder exactly 85 cc of water and take its temperature. What is the sum of the volumes of the water and the carbonate, separately? Add the weighed specimen of potassium carbonate to the water, dissolve by repeated inversion of the cylinder, closing the mouth of the latter with the hand, and read the volume of the solution (?) Read also the temperature of the solution immediately (?) Is there a change in volume, or in temperature, on dissolving two substances in one another?

What relation exists between the sign of the thermal effect when a substance is dissolved in a nearly saturated solution of the same substance, and the change of solubility with temperature [R 188-189]? What do you infer in this case?

*b* Examine the solubility curve of anhydrous sodium sulphate [R 132] (?) Will this compound give out or absorb heat in dissolving in water [R 188-189]? Verify your conclusion by trying the experiment (?)

*c* Repeat *a*, using about 25 g of ammonium chloride (sp gr 1.5) Make the same observations and answer the same questions

## CHAPTER IX

### HYDROGEN CHLORIDE AND CHLORINE

#### 45 Preparation of Hydrogen Chloride

*a* [Hood] Place small quantities of ammonium chloride, barium chloride, mercuric chloride, and sodium chloride in as many test-tubes, and add a few drops of concentrated sulphuric acid to each (?). Describe what happens in each case. Note the odor (?) and color (?) of the gas. Blow moist air across the mouth of the test-tube (?). Lower a glass rod dipped in ammonium hydroxide solution into each [Note 34, below] (?). Try the effect of heating. Remember that the solubility (physical) of the substance in sulphuric acid will largely determine the speed of the action. In case of difficulty, therefore, take a fresh sample of the solid, pulverize it finely, and shake with the acid for some minutes before heating and testing. Arrange the substances in the order of apparent activity (?).

*b* To a pinch of finely powdered sodium chloride add a strong solution of phosphoric acid and heat if necessary [R 142] (?). Test with ammonia as before (?). The above remark about solubility applies also to this case.

Why is hydrogen chloride displaced completely in *a* and *b* by these acids under these conditions [R 143]?

*c* [Hood] In a 250 c.c. flask (Fig 17), fitted with dropping-funnel (or substitute, 25 *b*) and L-shaped delivery tube, place about 30 g. of common salt. Use the shortest possible rubber connections here, and in 48 *b* (chlorine), as rubber tubing is destroyed by these gases. Admit concentrated sulphuric acid through the funnel. Collect the gas in three dry bottles



by upward displacement, allowing the tube to pass through a perforated square of paper or card so that the gas may not escape into the room. Cover, when filled, with glass plates and reserve for 46. Place about 10 c.c. of distilled water in a test-tube, attach a nozzle to the delivery tube, and allow the gas to bubble into this for a few minutes (?). Reserve the aqueous solution also for 46. Write equations for the two possible interactions of salt and sulphuric acid. Which of the two takes place under the above conditions?

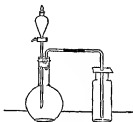


Fig 17

*Note 34* — The use of ammonia is not a specific test for hydrogen chloride. It can be used only for ascertaining the presence or absence of any one of several gases, usually of acidic character, which are capable of uniting with ammonia.

In writing the equation here, and whenever the same test is used, consider whether the interaction took place with the liquid on the rod (containing  $\text{NH}_4\text{OH}$ ), or with the gas ( $\text{NH}_3$ ) given off by this liquid. Note the odor of this gas (?).

#### 46 Properties of Hydrogen Chloride and of Hydrochloric Acid

*a* Invert one of the bottles of the gas in a dish of water (?). Relate this property to that observed on blowing moist air into the gas (45 *a*). If any gas remains, what should you expect it to be? Test your conclusion experimentally (?).

*b* Pour a little ammonium hydroxide solution on a strip of filter paper and plunge this into the second bottle (?). [Note 34, above]. Describe the difference between these fumes and those formed by the action of moist air upon the gas (45 *a*).

*c* Devise a way of proving, in a rough way, that the gas is heavier than air, and use the third bottle of gas for carrying it out.

*d* Six properties of hydrogen chloride have been considered

Make a list of these, and note opposite each whether it is a physical or a chemical property (?)

Perform the following experiments with the aqueous solution prepared in 45 c

*e* Test the solution with litmus paper (?)

*f* To a part add some zinc dust (?)

*g* To a part add a crystal of sodium carbonate [R 381] (?)

*h* Dilute the remaining portion of the acid solution with an equal volume of water and distribute it between three test-tubes. To one test-tube add a drop or two of mercurous nitrate solution (?), to the second a drop of lead nitrate solution (?), and to the third a drop of silver nitrate solution (?). After allowing the contents of each tube to settle, pour away the liquid, add water, and boil (?). Allow to cool, and note, by the appearance of crystals, which of the precipitates is soluble in hot water.

These precipitates are given, not only by hydrochloric acid, but by any chloride, and are, therefore, means of recognizing the presence of the chloride radical which is common to all chlorides.

**47 Theory of the Method Used in Preparing Hydrogen Chloride** To a saturated solution of sodium-hydrogen sulphate add pure concentrated hydrochloric acid (?). Add the acid a very little at a time to avoid over-rapid precipitation, and agitate between additions. The longer the operation takes, the better. Examine the result with a lens (?)

Write the equation for this action. What relation does this action bear to that in 45 c? What circumstances determine the direction of a reversible action [R 143-144]?

#### **48 Preparation of Chlorine [Hood]**

Experiments 48 b and 49 must be accomplished at one exercise. 48 a may be postponed to facilitate this.

*a* Prepare some strips of filter paper by dipping them in starch emulsion to which you have added one drop of potassium iodide solution.

Place small quantities of finely powdered manganese dioxide [R 158], potassium chlorate, lead dioxide, and pure litharge in as many test-tubes, and add a little concentrated hydrochloric acid to each. Notice the color (?) and odor (?) of the gas in each case. If no action takes place in the cold, apply heat. Dip into the gas in one of the test-tubes a strip of the prepared paper (?). How do you account for the difference in the behavior of the two oxides of lead? Do all compounds containing oxygen give free chlorine in this way? If not, state what is common to those which do and to those which do not (?).

b [Hood] Fit up a 250 c.c. generating flask, as in Fig. 17, with a dropping-funnel (or a substitute, 25 b) and an L-shaped glass tube attached to the exit tube. Use the shortest possible rubber connections here. Test the apparatus to see that it is air-tight. Place in the flask about 20 g. of dry potassium permanganate, and fill the globe of the dropping-funnel with diluted, concentrated hydrochloric acid (1 Aq. 3 acid). [CAUTION! Do not use any other acid, by mistake.] Allow the delivery tube to dip to the bottom of a small beaker containing a little sodium hydroxide solution. Now admit the acid drop by drop, regulating the flow so that too rapid a stream of gas is not produced. The complete displacement of the air in the flask will be recognized by the color of the contents and the fact that the bubbles of pure chlorine are completely absorbed by the sodium hydroxide.

When the air has all been displaced, fill three dry bottles and one dry test-tube with the gas by upward displacement, observing the following precautions. Provide a piece of stiff paper or card, perforated with a hole for the reception of the delivery tube, to cover the bottles during the filling, and cover the vessels with glass plates as soon as they are full. See that the delivery tube reaches to the bottom (why?) of each vessel during the filling. Replace the end of the delivery tube in the sodium hydroxide when all the vessels have been filled. When

the experiment is over, pour the contents of the generating flask into the sink in the hood, and not into one of the sinks in the open laboratory, and wash down with much water.

**49 Properties of Chlorine [Hood]**

*a* In one bottle of the gas scatter a pinch of finely powdered antimony [R 160] (?)

*b* Take a clean piece of sodium [From Instructor] and cut from it a very thin slice not more than one-half inch square (fingers and knife used in handling sodium must be dry!) Introduce this piece into a bottle of chlorine (?) and cover at once with a glass plate. Examine after half an hour. If any of the metal remains unattacked, scrape off the white deposit and place it upon a watch-glass, and throw the sodium into the sink in the hood. Add the material on the watch-glass to that in the bottle and dissolve in 2 c c of water. Allow the solution to stand in a watch-glass until it dries, and examine the crystals with a lens (?)

*c* Connect a glass nozzle with the illuminating-gas supply, and lower a small, burning gas-jet into the third bottle (?) Blow the breath into the bottle after withdrawing the jet (?)

*d* Fill a test-tube with hydrogen from a hydrogen generator, a Kipp's apparatus, or from the laboratory supply. Bring this tube mouth to mouth with a tube of chlorine and mix the gases by repeated inversion. (Take care not to expose the mixture to direct sunlight.) Hold the mouth of each tube to the Bunsen flame (?) Close the mouth of one tube quickly with the thumb, add a few drops of water, shake, and test the solution with litmus paper (?)

*e* Seven properties of chlorine have been considered. Make a list of these, and note which of them are physical and which chemical (?).

## CHAPTER X

### CHEMICAL EQUILIBRIUM THE HALOGENS

#### 50 Chemical Equilibrium in Double Decomposition

*a* When solutions of two substances, each composed of two radicals, are mixed, and no precipitate is observed, interaction nevertheless occurs

Place 10 c c of water in each of two test-tubes, add to one a single drop of ammonium thiocyanate solution, and to the other a single drop of ferric chloride solution. Now mix the solutions (?). The radicals are  $(\text{NH}_4)(\text{CNS})$  and  $(\text{Fe})(\text{Cl})_3$ . Write the equation for the action which may be assumed to have occurred. Is there any evidence that interaction has taken place? Which of the four is the colored substance? Use the mixture for *b*.

*b* When no precipitate is formed, is an action like the above complete? To answer this question, divide the mixture from *a* equally between four test-tubes. Keep one for reference. To the second add one drop of ferric chloride solution (?), and to the third a drop of ammonium thiocyanate solution (?). Interpret the result. Now add to the fourth tube a few drops of ammonium chloride solution (?) and explain.

What other action have we shown to be reversible (47)? All double decompositions of substances composed of radicals are reversible, like these two. They are also often far from complete, when, as in the present instance, precipitation does not occur. Why does precipitation tend to make the action more nearly complete?

#### 51 Another Incomplete Reaction

*a* Weigh out 1 g of calcium chloride (fused or gran.) and 12 g of oxalic acid. Dissolve each, separately, in 10 c c of

water, and heat the solutions to the boiling point. Add the oxalic acid solution to the calcium chloride solution, a little at a time, boiling for two minutes and allowing the precipitate to settle between the additions. When one drop ceases to produce any fresh precipitation in the clear part of the liquid, note what proportion of the original oxalic acid solution remains unused (?). Add this remainder, thus making sure that there is an excess of oxalic acid present, beyond that apparently necessary to precipitate all the calcium.

The radicals are  $(\text{Ca})(\text{Cl})_2$  and  $(\text{H})_2(\text{C}_2\text{O}_4)$ . Write the equation for the action (?). Write the name under the formula of each substance (?), and a downward arrow beside that of the precipitate (?). To what variety of chemical change does this one belong?

b Proceed now to find out whether this reaction is incomplete or practically complete. To do this, shake the mixture and pour it all on to a filter. Catch the filtrate in a clean test-tube, label it *F* (use in *c*). Set a vessel under the funnel, and wash the precipitate (calcium oxalate) with water. To do this pour water, a little at a time, from a test-tube on to the filter, so as to wash every part of it. When the filter has drained, set a test-tube under the funnel, puncture the filter-paper with a glass rod, wash the calcium oxalate through into the test-tube.

If the reaction was reversible, the equation, when read backwards, represents a possible chemical action. Name the interacting substances in the reversed action (?). To the calcium oxalate, suspended in water, add the required reagent (?). Was the action a reversible one? The conclusion may be confirmed as follows.

c If this reverse action occurs, it was in operation in the original mixture made in *a*. In that case, all the calcium could not have been precipitated, some must be present in the filtrate *F*, and the reaction was incomplete. The reaction may be com-

pleted by removing (or chemically altering) one product. Destroy the hydrochloric acid by adding to the filtrate *F* ammonium hydroxide a drop at a time and shaking (?). What does the result prove? Was this action more or less nearly complete than that in 50? Why?

#### THE HALOGENS

CHLORINE (Chap. IX) and the elements to be studied in this chapter form a group having very similar properties, and are called the halogens. Recall the facts about chlorine and hydrogen chloride, and use them as a guide in trying to understand the chemistry of the rest of the group. Remember particularly that chlorine is colored, has a powerful odor, and does not cause fumes in moist air, and that hydrogen chloride is colorless, and causes dense fumes in moist air. The corresponding substances throughout the group may be expected to present properties like these. Thus, the elements are all colored substances, the hydrogen compounds are all colorless and fume in moist air. The hydrogen compounds, hydrogen chloride, hydrogen bromide, etc., are known as the hydrogen halides.

**52 Preparation of Bromine [Hood]** Powder about 1 g of potassium bromide, mix it in the mortar intimately with about 2 g of pulverized manganese dioxide, and place the mixture in a test-tube. In a second test-tube dilute 2-3 c.c. of concentrated sulphuric acid with half its volume of water (add the acid, cautiously, to the water), and mix with the contents of the first test-tube enough of this solution to moisten the materials thoroughly, and no more. After allowing the mass to stand for a few minutes, apply a gentle heat to the tube, and note the color and behavior of the vapors evolved (?). Apply a strip of filter paper moistened with a starch-potassium iodide emulsion (48 a) to the mouth of the tube (?).

What other materials might be substituted for the potassium bromide in the above experiment?

### 53 Properties of Bromine

Shake up one drop of bromine [CARE Do not spill upon the hands] with 10 to 15 c c of water in a test-tube, and divide the solution ("bromine-water") between four test-tubes

a To one of these add 1-2 c c of ether, and shake (?) .Note the relative solubility of bromine in ether and in water, as displayed by the depth of color in each layer (40) To the second add carbon disulphide (?), and to the third chloroform (?), observing as before To about 10 c c of starch emulsion add a few drops from the fourth test-tube (?) [R 196 and see result of 57 b, below]

b Fit up an apparatus to generate a small amount of chlorine [Hood], using a side-neck test-tube instead of the flask in Fig 17 (p 51) If chlorine-water is available, it may be used instead of the gas

Dissolve a single, very small crystal of potassium bromide in a few c c of water in a test-tube Add several drops of carbon disulphide, and then pass a few bubbles of chlorine through the solution, or add a few c c of chlorine-water (?) Shake, and notice the appearance of color in the carbon disulphide (?) Infer from this result the relative activities of chlorine and bromine (?) Chlorine acts in the same way upon the bromides of all metals The result measures the relative affinity of chlorine and bromine for what elements?

The chlorine generator, if used, is required again in 57 c, which may be performed at once, before the apparatus is taken apart and cleaned Prepare also 5 c c of saturated chlorine-water, if not furnished on the side-shelf, cork it up in a test-tube, and set it aside in a dark place for use in 55 g and 60 a

### 54 Preparation of Hydrogen Bromide

a Pulverize about 1 g of potassium bromide, place it in a test-tube, and cover with concentrated phosphoric acid solution Notice the apparent slowness of the action on account of the insolubility (physical) of the compound in the liquid



(sodium bromide is much more soluble, and should be used, if available) Warm, if necessary Observe the odor (?), and insert a rod dipped in ammonium hydroxide solution (?) [Note 34, p 51]

For the action of sulphuric acid with a bromide, see 62 b

b Fit up a 250 c c flask with a dropping-funnel and exit tube, and connect with a U-tube (Fig 18) Render the apparatus air-tight and test it (?) Fill the U-tube with dry, broken glass or porcelain (why?), mixed with a little red phosphorus (why?)

2 Connect the other limb of the U-tube with a second, larger U-tube [Storeroom] containing about 10 c c of water Place about 5 g of red phosphorus mixed with twice its weight of sand in the flask, add 5 c c of water, and mix by shaking Pour into the globe of the funnel about 8 c c of bromine [EXTREME CARE Do not spill upon the hands (Note 16, p 2)] Allow the bromine to flow drop by drop

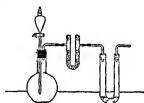


Fig 18

on to the phosphorus, and let the gas dissolve in the water in the second U-tube A large volume of air is expelled before the hydrogen bromide reaches the second U-tube Disconnect the second U-tube and reserve the solution for use in 55 How could hydrogen chloride be prepared in the same way?

Try the effect of moist air upon the gas issuing from the main apparatus (?) Hold in the gas a rod dipped in ammonium hydroxide [Note 34, p 51] (?)

55 Properties of Aqueous Hydrobromic Acid Divide the solution into seven portions and examine its behavior toward (a) litmus (?), (b) zinc in contact with a platinum wire (?), (c) silver nitrate solution (?), (d) mercurous nitrate solution (?), (e) lead nitrate solution (?), (f) powdered manganese dioxide (warm) (?) Boil c, d, and e, after pouring away the supernatant liquid and adding more water to each (?) Com-

pare these results with those found in the case of hydrochloric acid (46 *e, f, g, h*)

*g* To the seventh portion add a few drops of chlorine-water (53 *b*), a few drops of carbon disulphide, and shake (?) This result, and that in 53 *b*, indicate the relative affinities of chlorine and bromine for what elements (?), and how?

**56 Preparation of Iodine** Prepare a mixture of potassium iodide (1 g) and manganese dioxide (2 g) exactly as in 52, place it in an evaporating-dish, and moisten (2-3 drops) with sulphuric acid diluted with water (1 Aq 2 acid) Cover the dish with a watch-glass (partially filled with cold water to cool the surface presented to the vapors) and warm gently (very small flame) After a time examine the sublimate [Note 35, below] Expose a strip of filter paper, moistened with starch emulsion alone, to the vapors (?)

What other materials might be substituted for potassium iodide in preparing iodine?

*Note 35* — Stains upon the fingers caused by iodine may be removed by rubbing with sodium thiosulphate solution ("hypo")

**57 Properties of Iodine** Shake a small crystal of iodine vigorously [Note 35] with about 10 c c of water in a test-tube Pour the clear liquid off, dividing it equally between four test-tubes

*a* Add to one portion a few drops of chloroform, to another ether, and to a third carbon disulphide Shake each vigorously and note the relative solubility (estimated by depth of color) of iodine in water as compared with that in each of the other solvents (?)

*b* Take 15 c c of starch emulsion and add the fourth portion to it (?) Pour the mixture into the graduated cylinder and add water so long as a sample poured out into a test-tube continues to show an easily perceptible color Why is the use of starch considered to be a delicate test for iodine? Does it show the presence of iodine in combination (58 *b*)?

*c* Repeat 53 *b*, using a very small crystal of potassium iodide (?) Infer the relative activities of chlorine and iodine. The result measures the relative affinities of these two halogens for what elements?

*d* Repeat *c*, using potassium iodide, but substituting bromine-water for chlorine. In what order do the halogens stand, in respect to activity, and why do you place them in that order?

**58 Preparation of Hydrogen Iodide [Hood]**

*a* Repeat 54 *a* with potassium iodide or sodium iodide (?)

*b* Use the apparatus in Fig 18. Place in the flask a mixture of finely powdered iodine (20 g) and red phosphorus (1 g) intimately mixed in the mortar. Charge the U-tubes as in 54 *b*. Place a little water in the dropping-funnel (or substitute, 25 *b*), and allow the water to drop very slowly upon them (?). After the air has all been expelled, and the solution in the second U-tube has become sufficiently concentrated, remove the second U-tube. Test the issuing gas with moist a.s. (?) and with ammonia (?) as in 54 *b*. Hold in the gas a piece of filter paper dipped in starch emulsion alone (?). Explain (?). Reserve the contents of the second U-tube for use in 60 *a*.

**59 Preparation of Hydriodic Acid [Hood]** Place 5 g of powdered iodine with 50 c.c. of water in a small flask provided with a perforated cork and an L-tube extending to the bottom. Pass hydrogen sulphide from a Kipp's generator, or from the laboratory supply, through the mixture, loosening the cork once or twice at first to permit the air to be displaced by the gas, until the iodine is all gone and the solution no longer becomes brown on being shaken. Agitate constantly to hasten the process. Describe what happens. Towards the end of the operation, why does the iodine dissolve [R 445] (?) and why does the whole action then proceed much more rapidly? Warm and filter the solution.

Obtain a distilling-flask and condenser [Store-room] and distil the filtrate fractionally (Fig 19), collecting first the part that comes over at  $100^{\circ}$ , then the parts boiling between  $100-103^{\circ}$ ,  $103-106^{\circ}$ , and so forth. Use a very small flame, and be careful not to allow it to reach the walls of the flask above the liquid, or breakage will take place. A large flame may not only crack

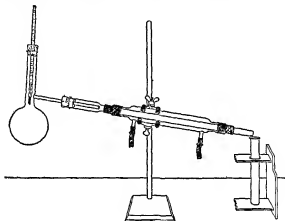


Fig 19

the flask, but may also cause the thermometer to show a higher temperature than it could acquire from the vapor alone. Stop when the liquid is nearly all distilled off. Note the highest temperature reached. Pour the residue into a test-tube and keep the series for use in 60 b.

What substance causes the brown color of the higher fractions and of the residue? Confirm your conclusion by a suitable test (57). How is this brown colored substance formed?

#### 60 Properties of Hydriodic Acid

a If 58 b was done, carry out the same experiments with the solution as were made with the solution of hydrobromic acid in 55 (?). Compare the results with those of 55 (?).

b If 59 was done, add silver nitrate solution to each of the fractions above  $100^{\circ}$  obtained in 59, using only a part of the liquid in the case of the two with the highest boiling-points. At what temperature did the most concentrated solution of hydrogen iodide come over? What peculiarity of aqueous hydriodic acid does the result indicate? What other solutions show the same peculiarity [R 145, 202, 206, 285, 348]?

Place a piece of zinc in the remainder of one of the higher fractions (?). Test the other with litmus paper (?), and then add pulverized manganese dioxide, and warm (?).

**61 Hydrogen Fluoride** Cover a square of glass with a thin layer of paraffin by warming it very cautiously far above a Bunsen flame and rubbing it on one side with solid paraffin. Moisten about 3 g. of fluorspar in a leaden dish [Storeroom] with concentrated sulphuric acid (do not cover with the acid). With the end of a file draw some design upon the paraffin-coated side, thus exposing parts of the glass to the action of the vapor. Now cover the leaden dish with the glass, paraffin side down, and set it in a moderately warm place, but not so warm that the paraffin is likely to melt. After half an hour or more, remove the glass cover, warm, and wipe off the melted paraffin with filter paper (?). Write equations representing the action, and state what becomes of each of the constituents of the glass [R 206, 427]. Try the test of a rod dipped in ammonium hydroxide and held over the contents of the lead dish (?). Does the gas fume with moist air? What substances, beside fluorspar, would serve the purpose of this experiment? Why could not hydrochloric acid or nitric acid be substituted here for sulphuric acid? What acid that we have employed could be used here?

How may fluorine be liberated from a fluoride? Why can it not be isolated from fluorides by the action of oxidizing agents, as was the case with the other halogens?

**62 Reducing Action of Hydrogen Iodide and Hydrogen Bromide [Hood]** In connection with this experiment, it must be kept in mind that an odor similar to that of rotten eggs shows the presence of hydrogen sulphide (59), and an odor of burning sulphur the presence of sulphur dioxide (14  $\alpha$ )

$\alpha$  Pulverize finely about 1 g of potassium iodide, place it in a test-tube, and moisten with one or two drops of concentrated sulphuric acid (?) If too much acid has been taken, start again. Warm gently. Investigate the result, which furnishes a mixture of gases, as follows

$\alpha$  Breathe across the mouth of the test-tube to ascertain the effect of the gas on moist an (?) What gases previously made showed the same behavior? What do you infer in this case? To confirm this conclusion, lower a glass rod dipped in ammonium hydroxide into the test-tube (?)

$\beta$  Is any characteristically colored vapor (?) mixed with the gas recognized in  $\alpha$ ? Can you observe any other property which identifies the substance? By what kind of chemical action could this colored substance be formed from the product identified in  $\alpha$ ? By what name is such a reaction known? Was there any corresponding product formed when sulphuric acid acted upon a chloride?

$\gamma$  Can you recognize still another (gaseous) product by its odor?

The work in  $\alpha$  and  $\beta$  and  $\gamma$  leads to the recognition of three gaseous or vaporous products. Do not attempt to put all of these in one equation. Construct one equation for the formation, from the original materials, of the gas recognized in  $\alpha$  (primary action), and make a second, separate equation for the formation of the other two products from the interaction of sulphuric acid with the gas recognized in  $\alpha$  (secondary action). What two properties of sulphuric acid (?) and what property of hydrogen iodide are illustrated by this set of observations?

In case the above directions are not followed implicitly, and

large pieces of potassium iodide are taken, or too much sulphuric acid is used, still another gas (sulphur dioxide) may be formed along with or instead of one of the above, and, in addition, a sublimate of free sulphur may be seen on the tube [R 277, par 2]

*b* Repeat the work in *a*, using powdered potassium bromide instead of the iodide, and answer the same questions

### 63 Identification of Halogen Compounds

*a* Imagine that there are given to you four white substances, and that you know them to be the fluoride, chloride, bromide, and iodide of some metal. State what experiments you would make, and what reasoning you would use, in order positively to identify the halogen constituents of each. In two of these cases, two different actions have been encountered in this chapter and might be used, and in the other two cases only one. Still another kind of action might readily be thought of [R 55, 155, 194, 227]. Negative results, say by showing that one is not a chloride, bromide, or iodide, and is therefore a fluoride, must be confirmed by a positive experimental test.

*b* If the four hydrogen halides were given you in gaseous condition in four jars, how should you proceed by chemical means to identify each?

## CHAPTER XI

### DOUBLE DECOMPOSITION    HYDROGEN PEROXIDE

#### 64 Radicals and Double Decomposition

*a* To a few drops of potassium chloride solution add silver nitrate solution (?). What kind of chemical interaction do salts usually show in solution [R 210. See Note 4, p. 1]? Write the equation for this action. How can we tell whether the precipitate is silver chloride, or potassium nitrate, or both? Which is it (Appendix IV)? What was the interaction of silver nitrate with hydrochloric acid (46 h)? To a few drops each of solutions of two other chlorides, such as ferric chloride and calcium chloride, add a little silver nitrate solution (?). Are these actions reversible [R 148]? Are they complete? Why?

To find out whether all substances containing chlorine give silver chloride in this way, try a few drops of potassium chlorate solution with the same silver compound (?). State now what radical a substance must contain in order that, with silver nitrate, it may yield silver chloride (?).

*b* To a few drops of silver sulphate solution add a solution of any chloride (?). To find out whether all substances containing silver yield silver chloride in this way, take a few drops of silver nitrate solution in each of two test-tubes. To the one portion add some ammonium hydroxide, and so obtain a solution of ammonio-silver nitrate  $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ . To the other add some potassium cyanide solution [CAUTION! POISON!] until the liquid is clear [Note 36, below], and so obtain a solution of potassium argenticyanide  $\text{KAg}(\text{CN})_2$ . Now add to each of



these a solution of sodium chloride (?) Is the silver radical present? Do all substances containing silver, when mixed with a chloride, give silver chloride? Which compounds alone give silver chloride by double decomposition?

c Which substances alone will, by addition of mercurous nitrate, give mercurous bromide (55 d)? Which substances alone will, by addition of silver nitrate, give silver iodide (60 a and b)? Which substances alone will, by addition of an acid, give hydrogen chloride (45)? Name the classes of substances which are composed of radicals, and commonly interact by double decomposition [R 210-211]

d Why was no precipitate observed when solutions of silver nitrate and potassium chlorate (64 a) were mixed? To answer this question, write the equation for the double decomposition which might occur, and consider the solubilities of the products (Appendix IV) (?)

*Note 36* — An insoluble body will not dissolve *as such* merely because of the addition of an excess of the precipitant, or even because of the introduction of a different reagent. When an insoluble body appears to go into solution, the phenomenon indicates that the substance added has interacted chemically with the insoluble substance and has produced a new substance which is soluble in water.

### 65 Peroxides.

a Prepare a solution of sodium peroxide by adding 2 g of this salt, a very little at a time, to 100 c c of cold water in a flask. Shake and cool (why? [R 459]) the mixture in a stream of water during the process. While still cooling the solution, add to it dilute sulphuric acid a few drops at a time until the mixture is acid (test?). What does the liquid now contain (50 a)? Divide the mixture into five parts and use them in b, c, d, e, and f.

b To one portion, contained in a small test-tube, add finely powdered manganese dioxide (?) Test the escaping gas for

oxygen (?) What rôle does the manganese dioxide play here?

c Prepare a solution containing free permanganic acid and sulphuric acid by adding a large excess of dilute sulphuric acid to 5 c c of potassium permanganate solution (equation?) Add some of this mixture to the second portion (from a) Test for oxygen the gas which comes off (?) What variety of chemical activity does the hydrogen peroxide show here?

d To the third portion add some starch emulsion containing a drop of potassium iodide solution (?) In writing the equation for this action, remember that the solution of hydrogen peroxide from a contained excess of sulphuric acid, which will interact with the potassium iodide (?) The product of this action then interacts with the hydrogen peroxide What variety of chemical activity does the hydrogen peroxide show here?

e Cut a long, narrow strip of filter paper, and moisten it with lead nitrate solution Pour 1 c c of ammonium sulphide solution into a test-tube, and hang the strip of paper in the test-tube until it becomes black What substance is formed? Now, dip the paper in the fourth portion of the solution from a (?) What practical application of hydrogen peroxide is here illustrated?

f To the fifth portion add 5 c c of ether (object of this [R 224]?) and shake, and then add one drop and no more of potassium dichromate solution and shake again (?) This is one of the most characteristic and delicate tests for hydrogen peroxide

State what substance here interacts with the hydrogen peroxide and how it is formed [R 224] Make no equation

g Suspend lead dioxide, barium dioxide, and pulverized manganese dioxide, separately, in water, add dilute sulphuric acid and shake for some time, cooling as in a Filter, and apply to each filtrate the test described in f (?)

What are the differences in behavior and constitution between a true peroxide (peroxidate) and those oxides which are sometimes called peroxides [R 223]?

*h* What are the radicals of potassium chlorate, hypochlorous acid, sodium peroxide, lead dioxide, potassium permanganate?

## CHAPTER XII

### IONIZATION AND INTERACTIONS OF ACIDS, BASES, AND SALTS

**66. Ionization** Name the four distinct methods by which we may ascertain experimentally whether a substance is ionized in solution or not, and may learn the extent of the ionization [R 214, 218, 239] (?) Define the term ionization, first in theoretical terms (?), and second in terms of the experimental evidence (?)

The degrees to which aqueous solutions of many substances are ionized are given in Appendix VI. Constant reference to this will be necessary in interpreting the observations in this and succeeding chapters

The experiments of this paragraph may be postponed until after the work in 67 or 68 has been done, if a set of the apparatus is not available at this moment



Fig 20

Obtain [Storeroom] an electrolytic cell (Fig 20). Half fill the cell with the substances named below in turn. See very particularly that the electrodes in the cell are not touching one another. Connect with the terminals on the lamp

\* The cell consists of a glass, flat-bottomed, specimen tube (about 75 x 22 mm) fitted with a two-hole rubber stopper in which a vertical groove has been cut to permit the escape of gases. The electrodes are pieces of tin about 10 cm long.

board\* (Fig 21b), and note whether the lamp glows or not (?) The cell is in series with the lamp and, if the lamp glows, the solution is a conductor. If it does not glow, the solution is a non-conductor. When the same experiment has been shown in the class-room, the result may be recorded here and the experiment omitted. Wash the cell and electrodes and wipe the latter very carefully after each trial.

The following eight substances, or solutions, show the behavior typical of the classes of materials to which each example belongs.

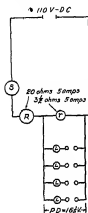


Fig 21a

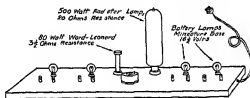


Fig 21b

After giving the result in your notes, name the class which is illustrated in each case.

If the substance is a conductor, what conclusion is to be drawn?

\* A storage battery of three lead cells or five Edison cells in series may be used, but is always in danger of being ruined by short-circuiting through carelessness. Protection by means of a fuse leads to continual interruptions of the work. Where direct current is employed in the lighting system, the best plan is to use the circuit through two resistances of such ratio to each other as to give the desired potential by the drop over one of them. Thus, if we place a 20-ohm, and a 3.5 ohm resistance on a 110 volt circuit (Fig 21a, diagrammatic), the potential drop over the lower resistance will be about 16.5 volts. If these resistances be of sufficient carrying capacity (say, 5 amperes), then four different current outlets may be provided — each one with plenty of current for one of the electrolytic cells previously described. Each of these outlets is in series with a small battery lamp, used as an indicator of the flow of current through the cell (Fig 21b).

Where alternating current only is available, a small rotary transformer, now commonly employed for charging automobile batteries, may be used.

in regard to the condition of the dissolved body? In each such case, write an equation showing the materials present in the solution, and write the name [R 236] under the formula of each substance (?)

- a* Dry, crystallized sodium chloride (?)
- b* Distilled water (?)
- c* Aqueous solution of sodium chloride (?)
- d* Diluted aqueous solution of sodium hydroxide (?)
- e* Diluted aqueous solution of hydrogen chloride (?)
- f* Aqueous solution of sugar (?) Now, dry the cell by washing first with alcohol and then with ether
- g* Toluene in the dried cell (?)
- h* Hydrogen chloride dissolved in dry toluene (?) What difference between water and toluene do *e* and *h* bring to light? Keep this solution coiled up in a dry test-tube for use in 70 *d*

#### 67 Ionic Materials

*a* Give the names and symbols (not forgetting the charges) of the three chief physical components, *i.e.*, distinct substances (in addition to water), present in the aqueous solution of sodium chloride [R 236] (?)

*b* Give a concise comparative statement of the specific physical properties (such as, color, molecular weight, solubility, behavior towards electrically charged bodies, physical state, etc.), of the ionic and the free forms of sodium, hydrogen, and chlorine (?)

68 Relations of the Molecular Substance to its Constituent Ionic Substances (in Equilibrium) The ions of an ionogen and the remaining molecules are in chemical equilibrium [R 215] What changes take place, respectively, when the solution is concentrated by evaporation and when it is diluted, as in *a*, below [R 249]? Can the proportion of molecules be increased otherwise than by concentrating the solution (see *b*, below) [R 250]? With substances like sodium chloride and hydrogen chloride these changes cannot be perceived by the

eye (why?) In the following instances (*a* and *b*) the ionic and molecular substances are both perceptible to the eye, and their relations as described above may, therefore, be studied very easily

*a* Examine a solution of potassium bromide. What is the color of bromide-ion? Take 0.5 g. of cupric bromide in a dry test-tube. Add two drops of water and agitate for some time (?). Then add more water, a drop or two at a time, agitating vigorously, and giving the substance time to dissolve, if it can, after each addition. Continue the addition of water cautiously until the substance has all dissolved, and afterward until the change in color is complete, and then stop. What is the color of the molecules of cupric bromide? What is the color of cupric-ion? Compare the color with that of cupric sulphate solution (?) and explain. Formulate the change which has been witnessed (?).

*b* Now take a fresh portion of cupric bromide and repeat the experiment as in *a*, stopping the addition of water at the green stage. Divide the mixture into two parts. To one add 2-3 g. of solid potassium bromide and shake vigorously (?). To the other portion add 4-5 g. of solid cupric chloride (?). Interpret the results.

The converse case, in which one of the ions is removed, and the dissociation is promoted, is discussed in *d*.

*c* Many ionic substances are colored, although the color does not always differ markedly from that of the molecules. Examine the following solutions, make a list of the ionic substances contained in them, with their formulæ and charges, and note the color of each kind of ion: cobalt chloride, potassium permanganate, potassium dichromate, chrome-alum (this last solution freshly made by dissolving the solid).

*d* Just as the union of ions to form molecules may be promoted by addition of a substance yielding a common ion (? 68 *b*), so the reverse of this, namely, the dissociation of mole-

cules into ions, may be promoted by the removal of one of the ionic materials. The removal of ions may be accomplished in several ways [R 250]

(1) By union of the ion with some other ion, when the molecules thus formed are insoluble. This case will be illustrated next (see 69)

(2) By union of the ion with some other ion, when the molecules thus formed, although soluble, are very little dissociated by water (see 71)

(3) By discharge of the ion and liberation of its material, through transfer of the charge to another substance (see 73)

(4) By union of the ion with some other material to form a compound ion, illustrated in 64 b

(5) By decomposition of the ion, as in 65 b, c

(6) By the mere change in the valence (amount of the charge) of an ion, for this converts it into another substance of the same material composition (see 166 a, 169, 197 b, 198 b)

(7) By discharge of the ion and liberation of its material through electrolysis. This was illustrated in 66 c, d, e

#### 69 Precipitation on Mixing Ionogens

a Place 3-4 c.c. of silver nitrate solution in a test-tube and dilute with water. Add potassium chloride solution cautiously and agitate continuously, until no further precipitation occurs (?). Filter, concentrate the filtrate by evaporation, and pour it into a watch-glass to crystallize (?). Two salts are obtained, one by precipitation and one by evaporating\* (see Fig 22)

Formulate the action (Fig 22). In doing this, show the

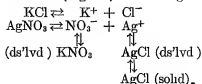


Fig 22



three main physical components of each of the original solutions and the relations of these components (in equilibrium) to one another in each case. Show also the molecular products formed when the solutions are mixed. Assuming that the solutions are approximately decimolar [R 124], ascertain the proportions in which the original components of the solutions are present before mixing (Appendix VI). Learn also to what extent the molecular products will be formed by union of the ions [R 247-8] (Appendix VI) and, in the case of an insoluble substance, how complete will be the precipitation (Appendix IV). On the basis of this complete information, complete the formulation [R 252], using heavy arrows to show main tendency in each equilibrium. Explain in detail, and one by one, in what way, and to what extent, each of the six original components is affected by the results of mixing.

Name the components of the filtrate and explain how each is affected by the evaporation and crystallization.

How does the formation of the precipitate of silver chloride illustrate 68 *d* (1)? Upon what factor does the completeness of the change depend? Is, or is not, silver chloride a highly ionized substance [R 253]?

Aside from double decompositions, what means have we for learning of what radicals a salt (like silver nitrate) is composed?

*b* To a little cupric sulphate solution in a test-tube add sodium hydroxide solution (?). Exactly as in 69 *a* (second part), formulate, study and explain the whole action. How does this illustrate (1) of 68 *d*?

To what classes of ionogens do the four molecular substances respectively belong?

*c* To a little cupric sulphate solution add a little dilute hydrochloric acid (?). In what respects does the result differ from those in *a* and *b*, and why? Can any acids be prepared by precipitation, and if so, which [R 429, 432]?

In future, formulate all ionic actions in a way indicated in *a*.

**70 Bases and Acids Hydroxide-ion and Hydrogen-ion. Indicators**

*a* Examine distilled water in respect to (a) taste, (b) behavior with litmus, (c) conductivity (done already, 66 *b*)

*b* Dissolve a small piece of sodium hydroxide in water and examine the solution in respect to (a) taste, by diluting a little and tasting one drop, (b) behavior with litmus, (c) behavior with phenolphthalein, (d) conductivity (see 66 *d*) These properties belong to aqueous solutions of all bases. Aside from the water, what component alone is common to all solutions of bases, and has the above properties? Name this component and give its formula (?)

*c* Examine an aqueous solution of hydrochloric acid in respect to (a) taste, (b) behavior toward litmus, (c) behavior with phenolphthalein, (d) conductivity (see 66 *e*), (e) action on a piece of marble, (f) action on an iron nail (clean this with the file before use). These properties are shown by all aqueous solutions of acids. Aside from the water, what component alone is common to all solutions of acids, and has these properties? Name and give the formula of this component (?)

*d* Take the solution of hydrogen chloride in toluene (66 *h*) and examine it in respect to (a) conductivity (done already, 66 *h*), (b) action on a piece of marble, dried in advance by heating in a dry porcelain dish for a few moments, (c) action on an iron nail (clean as before). Be sure that perfectly dry vessels are used in these experiments. What substance identified in *c* is absent from this solution? What difference between water and toluene, as solvents, does this result indicate? In what three other respects would the two solutions of hydrogen chloride be found to differ?

**71 Ionic Chemical Changes I Union and Disunion of Ions. Neutralization (Union of  $H^+$  and  $OH^-$ )** (Two students working together) A considerable chemical change may occur not only in precipitation (see 69), but also when ions unite to form

a substance which, although soluble, is very little ionized by water. Such changes are illustrated in 71 and 72.

Weigh out 5 g (laboratory scales) of potassium hydroxide, dissolve it in a little distilled water in the graduated cylinder, add water until the total volume is 50 c c, and pour the clear solution into a burette (Fig 4, p 8). Measure 10 c c of concentrated hydrochloric acid in the graduated cylinder, mix it in a small beaker with 50 c c of distilled water, and pour this into a second burette. Now, into a small beaker or flask run 15 c c of the acid solution from the second burette, and then add to it two drops of phenolphthalein solution. Place the vessel under the first burette, read the level of the liquid in the burette, and allow the alkali to run into the acid drop by drop, stirring constantly, until the last drop confers the faintest perceptible pink tinge on the whole solution. If you do not at first succeed in stopping at the right point, repeat the experiment. Note the volume of alkali used. Concentrate the solution on the sand bath until a drop deposits crystals on cooling, and then remove the dish from the sand bath promptly and set it aside.

When sufficient crystals have appeared, dry them with filter paper and examine with respect to (a) form, (b) taste, (c) exposure to moist air, (d) action of a solution on litmus, (e) conductivity of aqueous solution (done already, 66 c). Construct a table comparing the substance in these respects with the materials from which it was made. Compare the substance with potassium chloride. How should you determine whether a substance obtained in this way contained "water of crystallization" or not? Make the necessary experiments (?). Wash out the burettes.

Following the directions in 69 *a* (second par.), formulate, study, and explain the whole action. Note, however, that there is here no insoluble substance. Show how this experiment illustrates 68 *d* (2).

Express the change involved in every neutralization of highly ionized substances by means of the simplest equation [R 254] How may neutralization be defined, in terms of the hypothesis of ions? How may it be defined, taking account of *all* the facts, but omitting all reference to ions?

Calculate the approximate concentration, in terms of a normal solution as unity, of the potassium hydroxide solution used above (?) From the volumes of alkali and acid used in neutralizing, calculate the concentrations of the diluted hydrochloric acid (?), and of the concentrated acid employed to make it (?), expressing the concentrations in terms of a normal solution Calculate the number of grams of hydrogen chloride per liter in the dilute and concentrated acids, respectively (?)

#### 72 Neutralization of Slightly Ionized and of Insoluble Substances

*a* Consider the degree of ionization of acetic acid (Appendix VI) To neutralize 1 liter of normal acetic acid, would more or less alkali be required than to neutralize 1 liter of normal hydrochloric acid? In what way, precisely, would the details of the change be different in the case of acetic acid [R 255]? Name some of the consequences of this difference [R 255]

*b* Dilute a few drops of cupric sulphate solution with much water and add excess of sodium hydroxide solution (?) Fit a filter paper properly into a funnel (Fig 6, p 11) Filter the mixture, and wash the precipitate (?) and filter paper repeatedly, with distilled water to remove soluble substances Now place a clean test-tube below the funnel, perforate the bottom of the filter paper, and wash the precipitate through into the test-tube by means of a stream of water from the wash-bottle To the suspended cupric hydroxide, cautiously add dilute hydrochloric acid in amount just sufficient to give a clear liquid Concentrate the liquid on the sand bath until a drop, removed to a watch-glass, shows signs of crystallizing when cold Then

remove the dish promptly from the sand bath and allow it to cool. Examine the crystals (?)

Formulate this action as in 69 *a*, taking account, however, of the fact that one of the interacting substances is an "insoluble" solid [R 272]. Describe in detail the stages through which the final production of solid cupric chloride is accomplished.

To what class of ionic chemical changes [R 258] does the foregoing action belong? Answer the same question in regard to the precipitations of salts in 69.

### 73 Ionic Chemical Changes II Displacement

*a* Place several pieces of granulated zinc in a dilute solution of cupric sulphate and set aside until the change is complete (test?). Occasional agitation will hasten the change (why?). Filter. What is the precipitate [R 259]? Preserve the filtrate.

Before examining the filtrate, take a few drops of cupric sulphate solution and a like amount of zinc sulphate solution in two test-tubes. Dilute each solution with water, and add to each ammonium sulphide solution (?). What is the precipitate in each case, and what ions are required to form it?

To the filtrate from the first part of this experiment add ammonium sulphide solution (?). What ions were present in the filtrate? What changes did the metallic zinc and the cupric ions, respectively, undergo in the first part of the experiment? Formulate this change in an equation. In the course of this experiment, what becomes of the molecular cupric sulphate (68 *d* (3))?

What substances could have been substituted for the cupric sulphate without affecting the result so far as the consumption of zinc and the precipitation of copper were concerned? What substances, beside zinc, would have precipitated copper (Appendix VII)? What other elements, beside copper, are displaced by zinc?

Which one of the elements displaced by zinc did we prepare

in quantity by an action like the present (18)? Formulate this action in terms of ions. What were the products of the action of zinc upon concentrated sulphuric acid (16 *d*)? What is the chief component of this form of the acid (Appendix VI)? If this component interacted with the zinc, to what class of chemical changes did this action belong?

*b* Formulate the actions in 16 *a* in terms of ions. Explain the differences in activity of the various metals [R 260]

*c* Examine your notes on Chap. X. Formulate the following actions in terms of the hypothesis of ions

Free chlorine and bromide-ion (53 *b* and 55 *g*)

Free chlorine and iodide-ion (57 *c* and 60 *a*)

Free bromine and iodide-ion (57 *d*)

Free iodine and sulphide-ion (59)

Arrange these four elements in a series similar to the electromotive series of the metals (Appendix VII). Where should you place fluorine in this series [R 205]? Indicate the approximate position of oxygen [R 202, 205]?

**74. Ionic Chemical Change III, IV, V** In addition to union or disunion of ions (I), and displacement (II), there are three other ways in which ions may undergo chemical change [R 258-259]

Electrolysis (III) was illustrated in 66 (?)

Formation or decomposition of a compound ion (IV) was illustrated in 48 *a* and *b*, in 64 *b*, and in 65 *c* (?)

Change in the charge on an ion (V) was illustrated in 48 *a* (?)

Define each of these three classes of ionic chemical change and formulate the illustrations anew so as to show how the actions cited belong to the class illustrated (?)

Re-examine the seven ways in which ionic substances are removed, and dissociation of the parent molecules is promoted (68 *d*), and indicate that one of the five classes of ionic change to which each of the seven belongs (?)

**75 Non-Ionic Actions** In previous class-room and laboratory experiments we have observed the formation of ionogens in other ways than those illustrated in this chapter. These ways are non-ionic, or not distinctly ionic. Give illustrations of such of these ways as you recall: acids, two ways, bases, one way, salts, four ways, together with the reference numbers of the laboratory experiments in which they occur (?)

## CHAPTER XIII

### SULPHUR

#### 76 Sulphur

a Place about 0.5 c.c. of powdered roll sulphur in a dry test-tube, add 2 c.c. of carbon disulphide and shake (?). Pour the solution into a watch glass and set it to evaporate [Hood] away from all flames.

Examine the crystals with the eye and with a lens and make a drawing of two of them (?). Are they brittle or soft? Color? Are they transparent? After 24 hours (or more), are they still transparent?

b Fold a filter-paper as if for filtration, and put water in a large beaker. Half fill a dry test-tube with roll sulphur. Hold the test-tube with a clamp and melt the sulphur. Heat gently, turning the tube in the flame. Dark brown patches show overheating at these points — melted sulphur is pale straw-color.

Hold the filter-paper by the edge at the three-fold side and pour the melted sulphur into it. Watch the crystals grow. When crystals have formed at the surface and reached the center, pour the remaining liquid sulphur promptly into the beaker of water, and open up the paper immediately.

Examine the crystals with the eye and with the lens and make a drawing of two of them (?). Are they brittle or soft? Color? Are they transparent? After 24 hours (or more), are they still transparent? If not, into what form of sulphur have they turned? Explain the change in appearance (?).

Examine the part that was poured into water. Is it brittle or soft? Dry a small piece of it and shake it with 1 c.c. of carbon disulphide (?).



c In the same test-tube place 10 g of roll sulphur and melt. Continue heating until the sulphur boils and note the changes in color and fluidity which occur (?) If the vapor catches fire, allow it to burn. Pour the boiling sulphur into a large beaker of water, moving the tube about.

Examine the product. Is it crystalline? Is it brittle or soft? Is it transparent? After 24 hours (or more) is it still transparent? After 24 hours (or more), dry a part of it and shake with a little carbon disulphide (?) To find out whether any has dissolved, pour part of the liquid on to a filter, catch a few drops of the filtrate on a watch glass, and allow them to evaporate [Hood] away from flames (?)

What is the insoluble material? Color? Examine with a lens (?) Is it crystalline?

What would have been the result if the boiling sulphur had been allowed to cool slowly, instead of being chilled in water?

#### 77 Sulphides of Metals

a Place about 2 c.c. of roll sulphur in a dry test-tube and fasten the tube upright in the clamp on the stand. Boil the sulphur and then drop into the tube a strip of copper foil (?). Does the temperature of the copper change noticeably? Was it heated thus by the flame, the sulphur vapor, or what?

Remove the strip of copper and describe the properties of the product (?). Name it (?) and write the equation (?)

b Mix thoroughly in the mortar 1 c.c. of iron powder with 15 c.c. of powdered roll sulphur. Place the mixture in a test-tube and clamp the latter on the stand. Heat the lower part of the material and, when the reaction begins, withdraw the flame.

Was the temperature at any time higher than that which the flame could have produced? What was the source of the heat? Describe the product when cold (?). Name it (?), and write the equation (?) Keep it for use in 78 a.

c Recall and record here a case of the union of sulphur with a metal which was observed previously (8 a). Under the same

conditions (pressure, temperature, contact), does mercury combine more or less readily with sulphur than with oxygen? Give reasons for your answer (?)

Does sulphur appear to have about the same activity as has oxygen, or much more or much less?

#### 78 Hydrogen Sulphide [Hood]

a Place about 1 g of ferrous sulphide in a test-tube and add a little dilute hydrochloric acid (?) Note the odor of the gas, and apply to it a strip of filter paper dipped in lead nitrate solution [R 577] (?)

b Using ferrous sulphide and hydrochloric acid, generate hydrogen sulphide, using either the apparatus in Fig 10 (p 22) or a special generator. Connect with the exit tube a glass nozzle. When the air has been displaced, set fire to the gas. Describe the color of the flame (?) Hold a porcelain dish in the middle of the flame for a few moments (?) What substance is deposited, and must, therefore, exist uncombined in the interior of the flame? What other substance does this justify us in assuming to be liberated in the same region? What do these facts indicate regarding the stability of the gas when heated, and the difficulty, therefore, of making the compound by the direct union of its elements? What are the products of the complete combustion of the gas, and in what two stages does this combustion take place? Make equations showing both stages (?)

#### 79 Properties of Aqueous Hydrogen Sulphide I [Hood]

a Take about 15 c.c. of water in a carefully cleaned test-tube and, using a clean piece of glass tubing to deliver the gas, saturate (test? Note 37, below) it with hydrogen sulphide. Test the solution with litmus paper [R 269] (?) Pour one-third or less of the solution into another test-tube and boil this portion vigorously, noting from time to time the odor of the vapor (?) Can this gas be driven off completely by boiling? Does hydro-

gen chloride solution behave in the same way or differently [R 145]?

*b* Divide the remainder of the solution into two parts and add 2-3 g of iron dust (pulverized non) to one of them. Shake vigorously and then allow the mixture to stand (?). After an hour collect the insoluble matter upon a filter [Note 39, p 116] and wash until it no longer smells of hydrogen sulphide. Transfer the precipitate to a test-tube by puncturing the paper and washing through. Add dilute hydrochloric acid to the solid product and note the odor (?). What substance must have been present in the precipitate, and how was it formed? Account for the extreme slowness of the action of non upon the solution of hydrogen sulphide [R 269]

*c* Allow the third portion of the solution made in *a* to stand for some days exposed to the air (?). Explain the turbidity (?).

*d* If 59 was performed, record here the action which took place (?). If 59 was not performed, place a single crystal of iodine in 5 c c of water and saturate (test? Note 37, below) the liquid with hydrogen sulphide [R 201] (?).

What ionic substance is shown by the first part of 79 *a* and by 79 *b* to be present in the solution of hydrogen sulphide [R 269]? Explain the actions in *c* and *d* in terms of ions.

*e* To 2-3 c c of potassium dichromate solution add dilute sulphuric acid in large excess (?). What change may be assumed to have taken place? Now saturate (test? Note 37, below) the mixture with hydrogen sulphide (?). What are the colors of the solution and of the precipitate, respectively? Show that two kinds of ionic chemical change are here illustrated (?).

*f* Take 2-3 c c of potassium permanganate solution and treat exactly as in *e* (?). Answer the same questions (?). What chemical property of hydrogen sulphide is illustrated in

*Note 37* — To learn whether a liquid is saturated with a gas, withdraw the delivery tube while the gas is issuing, cover the mouth of the vessel quickly with the thumb or the palm of the hand in such a way that the gas above the liquid has no time to escape (why?), and shake vigorously. If the thumb now adheres to the mouth of the vessel, the liquid is not yet saturated (why?) If the liquid is saturated, what will be the pressure of the gas over it after shaking [R 128]? If air is allowed to displace the gas over the saturated liquid, what effect will be observed on shaking as described above, and why?

### 80 Properties of Aqueous Hydrogen Sulphide II Sulphides [Hood]

*a* What was the reaction of aqueous hydrogen sulphide towards litmus (79 *a*)? What ionic substances are present?

*b* Take about 6 c.c. of sodium hydroxide solution and saturate (test? *Note 37*) it with hydrogen sulphide (?) Use in *c*, *d*, *e*, and *f*. How should you proceed to prepare neutral (or normal) sodium sulphide (solid)?

*c* To a few drops of the solution prepared in *b* add dilute hydrochloric acid (?) (see 81 *b*)

*d* To a few drops add some bromine-water (?)

*e* To a larger portion of the same solution add a little powdered iodine sulphur and shake from time to time. Is sulphur soluble in water? What is here to be inferred [*Note 36*, p. 67]? When the solution has become very yellow (?) in color, filter. Acidify the filtrate with dilute hydrochloric acid (i.e., add more than an equivalent amount of the acid) (?) Recall an experiment with iodine which resembles this experiment with sulphur (?)

*f* Allow the remainder of the solution from *b* to remain exposed to the air for several days (?) When a change in color has occurred, add dilute hydrochloric acid in excess (?) Explain

*g* Take five clean test-tubes and obtain 2–3 c.c. of the solution of each of the following substances. Dilute each specimen with 10–20 c.c. of water and saturate (test?) with hydrogen

sulphide (a) Cupric sulphate (?), (b) Lead nitrate (?), (c) Cadmium sulphate (?), (d) Ferrous sulphate (make a solution of ferrous-ammonium sulphate [R 245] and use it for this [Note 38, below]), (e) Zinc acetate (?)

Explain the precipitation in terms of ions

Pour away a part of the contents of each test-tube, including a part of the precipitate, add a large excess of dilute hydrochloric acid, and shake (?) Explain the results Divide the metallic sulphides obtained in this experiment into two classes, and characterize those classes

What property of hydrogen sulphide has been illustrated in a, b, and g

*Note 38* — Ferrous-ammonium sulphate [R 245] is preferred to ferrous sulphate because it becomes less rapidly opaque through oxidation by the air In making equations, disregard the ammonium sulphate

### 81 Ionic Chemical Changes Formation of an Inactive Acid

a To 2-3 c.c. of sodium acetate solution add an equivalent amount of dilute sulphuric acid, and warm gently One product may be recognized by its odor (?)

Formulate, study and explain this action according to the directions in 69 a (second part) Write a simple equation expressing the chief change which occurs

b Consider the action between sodium-hydrogen sulphide and hydrochloric acid in 80 c Formulate, study and explain this action as in 69 a (second part), modifying the scheme of formulation to suit the case Does the escape of the hydrogen sulphide assist materially in making the action more nearly complete [R 272]? Does it assist at all? What physical property does the escape of the hydrogen sulphide as a gas show this substance to possess?

c Make a single general statement describing all the cases in which, when ionogens are mixed, and no precipitation or volatilization occurs, a fairly complete chemical change will nevertheless take place (see 71)

Give a list of acids (Appendix VI) which might be formed in accordance with the principle embodied in your statement

Could any bases be formed in accordance with the same principle? Illustrate (Appendix VI) Could any salts be so formed (Appendix VI)?

### 82 Hydrolysis

*a* Dissolve a single crystal of sodium sulphide in water, and test the solution with litmus paper (?) What ionic substance causes this reaction? Which of the two substances taken is capable of furnishing this ion? Formulate the interaction of the two original substances and explain it [R 271]

*b* Test with litmus paper the solution of sodium carbonate (?) Explain (Appendix VI) Of what sorts of radicals must a normal salt be composed in order that the solution may show an alkaline reaction [R 271]?

*c* Test with litmus paper the solutions of cupric sulphate (?) and ferric chloride (?), and account for the result [R 437] Of what sorts of radicals must a normal salt be composed in order that the solution may show an acid reaction? Why is sodium chloride solution neutral? Define hydrolysis (?)

### 83 Sulphur Dioxide

*a* Touch with a warm platinum wire a bit of sulphur, and bring the wire with the adhering sulphur again into the flame. Withdraw, and note the color of the flame of the burning sulphur and also the odor (?)

*b* Heat in a hard glass test-tube a few particles of non pyrites. What is the sublimate? What gas is evolved?

*c* [Hood] Place a small piece of copper in a test-tube, cover it (and no more) with concentrated sulphuric acid, and fix the tube in a clamp on the stand. Place the bulb of the thermometer in the acid, heat continuously, and note the temperature at which chemical action becomes apparent(?)

Remove the thermometer and smell the gas (?). Heat the materials with a small flame while proceeding with *d*. Then set the tube aside and, the next day, examine and describe all the contents (?).

*d*. [HOOD] If sulphur dioxide gas is not furnished in the laboratory from cylinders of the liquid,\* it may be prepared for use in 84 or 89 as follows. Fit up a flask (250 c.c.) as in Fig. 17 (p. 51). If 84 is to be performed, a gas washing-bottle (Fig. 23) will be required to dry the gas, and will contain enough concentrated sulphuric acid to immerse the longer tube to a depth of half an inch. Attach the longer tube of the bottle by rubber tubing to the generating flask. Place about 15 g. of sodium bisulphite in the flask. Test the apparatus to see that it is air-tight. Dilute some concentrated hydrochloric acid (1:1) and place it in the funnel.

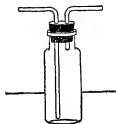


Fig. 23

**84. Molecular Weight of Sulphur Dioxide** [Quant. Hood] Clean and dry a 250 c.c. flask and provide it with a tightly fitting cork. Weigh the flask and cork. This gives the weight of the flask filled with air. Now fill it completely with sulphur dioxide, by upward displacement of air, cork, and weigh again. To insure its being full, repeat this operation till no increase in weight occurs. Finally, allow the gas to escape and determine its volume. To do this, use the graduated cylinder and fill the flask with water up to the cork (?). Observe the temperature and pressure of the atmosphere (?). Correct the volume to 0° and 760 mm. pressure.

To obtain the weight of the empty flask and its cork, subtract from the weight of the vessel filled with air the weight of a volume of air equal to the corrected volume (1 liter of pure, dry

\* If the gas is not so furnished, 83 and 84 should be taken up after 88.

air weighs 1.293 g under normal conditions, or the G M V holds 28.955 g of air)

The difference between this weight of the empty flask and that of the flask filled with sulphur dioxide is the weight of the gas. Using the volume of the flask at normal conditions, calculate the weight of the G M V (22.4 l) and of 1 l of sulphur dioxide (?)

Enumerate carefully all the sources of error to which you should expect this way of determining the density of a gas to be liable (?) In doing this, consider each detail of the operation very critically

Temp °	Barometer (corr)	mm
Vol of flask		c c
Vol of flask, 0° and 760 mm		c c
Wt of flask + air		g
Wt of air (calc)		<u>g</u>
Wt of flask, empty		g
Wt of flask + SO <sub>2</sub>		g
Wt of flask, empty		<u>g</u>
Wt of SO <sub>2</sub>		g
Wt of 22.4 l SO <sub>2</sub>		g

**85 Preparation of Sulphuric Acid** (Two students working together) Obtain a distilling-flask (25 c c), rubber connections for a safety bottle, a screw-clamp, and a Chapman pump from the store-room. Fit up with your one-liter bottle the apparatus as in Fig 24. Charge the hard glass tube with about 10 g of granular pyrite,\* and place a small, loose plug of asbestos just beyond the pyrite to retain any unburnt sulphur. Put into the distilling-flask about 10 c c of pure concentrated nitric acid. The safety bottle, half filled with water to show the rate at which air is being drawn through the apparatus, is attached to the water pump. The total air admitted is regulated by the

\* In case very pure pyrite is not available, it is better to depart from the common manufacturing process by substituting a boat containing a little sulphur.



screw-clamp between the pump and the safety bottle, while the proportions which pass over the pyrite and which carry over the nitric acid vapor, respectively, are regulated by pinching one of the tubes with the finger and thumb

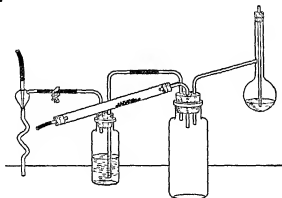


Fig. 24

First heat the pyrite in a very slow stream of air until the sulphur burns. Then warm the nitric acid and, by pinching the tube admitting air to the pyrite-burner, divert part of the air current so that it may carry over a little of the vapor of the acid. Heat the pyrite strongly and continuously. Repeat the introduction of air laden with nitric acid at intervals, whenever the disappearance of the red fumes in the bottle shows that a further supply is needed.

• After a crust of white crystals (?) has formed in the bottle (there may be considerable delay before crystallization starts), remove the attachments and blow the gases from the interior by means of the air blast. If crystallization fails to begin after a reasonable time (note that an interaction even between the molecules of gases may be slow, in spite of the completeness of the mixing), the cause is either the introduction of too much

water along with the nitric acid, or the high temperature produced by the chemical actions taking place in the bottle. Removing the attachments and cooling the bottle in a stream of water frequently brings crystallization about.

Add 4-5 c.c. of water and wash down the crystals with it. Describe all that happens (?). If more of the product is required, the apparatus may be connected up again and a further supply of sulphur dioxide drawn into the bottle, and subsequently more nitric acid vapor can be added. Finally any remaining crystals may be decomposed by water.

Filter the liquid in the bottle through a very small filter paper into a dish, rinsing the bottle with 2-3 c.c. of water, and evaporate on the sand bath [Hood] until the liquid begins to fume strongly (?). This will remove any nitric or nitrous acid that it may contain. Use the result for 86 a and b.

#### 86 Properties of Sulphuric Acid

a Dip a match-stick into the liquid from 85 (or into a few drops of concentrated sulphuric acid), and make marks on a sheet of paper. Place both paper and stick in a warm place (?). What property of the acid is here observed?

b After the acid prepared in 85 is cold, dilute it with 2 volumes of water. Test the solution with litmus paper (?). To 2-3 drops of the acid add barium chloride solution (?). To learn whether the action is easily reversible, add pure hydrochloric acid to the mixture (?). The formation of this precipitate, and its insolubility, furnish a distinctive test for what radical? Which substances contain this radical? To the rest of the acid add a minute amount of cupric oxide (pulv.) and warm gently for one minute or more (?). Can an oxide of a metallic element be formed in presence of sulphuric acid? What property of sulphuric acid is shown in b?

c Pass a current of hydrogen sulphide through 2-3 c.c. of concentrated sulphuric acid. Note the odor (?) and precipitate (?). What property of sulphuric acid is shown in c? What

other evidence of this property have we previously observed (see 16 *d* and 62)?

*d* Place a small piece of sulphur in 2-3 c c of concentrated sulphuric acid, and heat (?) Note the odor (?)

*e* Heat a little charcoal with sulphuric acid and note the odor (?) What property of sulphuric acid is shown in *d* and *e*? Why would not dilute sulphuric acid show this property?

*f* [HOOD] Take 2-3 c c of concentrated sulphuric acid in a test-tube. Suspend a thermometer so that the bulb is completely immersed in the acid. Heat the contents of the tube by means of a small flame and note the temperature at which any effect (?) is observed, and that at which it is conspicuous. Relate this temperature to that observed in 83 c. [CAUTION! During the heating remember that, if the tube should crack, the hot acid may splash on the clothes and hands and produce severe burns. Hold the burner in the hand, and place a large beaker below the test-tube. Exercise proper caution. Be careful not to wash out this tube until the acid has cooled.]

#### 87 Sulphuric Acid as a Dibasic Acid

*a* (Two students working together.) Fill a burette with a solution of potassium hydroxide made as in 71. Add 15 c c of concentrated sulphuric acid slowly to 35 c c of water in a beaker, and fill another burette with the diluted acid, when cold. Ascertain as in 71 what volume of the alkali will neutralize 5 c c of the acid. Concentrate the mixture in an evaporating dish to about 10 c c, remove the dish from the water bath, and allow the resulting solution to crystallize. Dry the crystals on filter paper. To a second portion of the acid (use no phenolphthalein. Why?), twice as great as before, add exactly the same amount of the alkali. Evaporate to about 5 c c and treat as before.

Compare the two lots of crystals as regards (a) form, (b) taste, (c) reaction of their solution towards litmus. Confirm by studying the same properties of the pure substances. Explain

the differences in these three respects between your own preparations and the pure ones, if any are observed. Explain, in terms of the hypothesis of ions, the difference in the reactions of the two products towards litmus.

Formulate, study, and explain the actions, as in 69 *a* (second part). Take the components of the original solutions [R 287] one by one, and describe what happens to each, (a) during complete neutralization, (b) during semi-neutralization in the second part of the experiment.

What would be the effect of heating perfectly dry specimens of each of the salts [R 285]?

How many grams of potassium-hydrogen sulphate are required to give 1 liter of a solution of normal concentration in respect to (a) potassium-ion, (b) hydrogen-ion, (c) sulphate-ion?

*b* Make a solution of sodium bicarbonate and test it with litmus paper (?) and with Congo red paper (?). Why do some acid salts show little or no acid reaction towards indicators?

Define carefully, and illustrate, the terms normal (neutral) salt, acid salt, and basic salt [R 245].

**88 Sulphates** Place some ferric sulphate in a porcelain crucible supported on the clay triangle, and heat strongly [Hood] with the blast-lamp, continuing the heating after all the water has been driven off (?). What are the properties of the vapor given off (?), and what is it? What is the residue? Relate this result to that in 86 *f*. Recall the action of heat on dehydrated gypsum (30). Classify the sulphates in accordance with this distinction.

**89 Properties of Sulphurous Acid** [Hood] Use a stream of sulphur dioxide from a cylinder of the liquefied gas, or from the apparatus described in 83 *d*. Boil half a test-tube full of water for two minutes and set it aside to cool for use in *c*.

*a* Pass a stream of sulphur dioxide for a few minutes into a test-tube full of water. Test the solution with litmus paper (?).

What compound is present in the aqueous solution of the gas? Note also the odor of the liquid (?) Formulate the interaction, showing all the substances present. Divide the solution into three portions.

*b* Boil one portion persistently in an evaporating dish [Hood] noting from time to time the odor and reaction towards litmus (?). In respect to the result, does the solution of this gas resemble that of hydrogen sulphide, or that of hydrogen chloride?

*c* Pass sulphur dioxide through the water that was boiled and to this add barium chloride solution (?). To ascertain whether this action is easily reversible, add excess of pure hydrochloric acid (?).

*d* To the second portion from *a* add bromine-water (?) until the color is permanent (?). Now add barium chloride to the mixture (?) and then pure hydrochloric acid (?).

What chemical properties of sulphurous acid are illustrated in *a*, *b*, *c*, and *d*, respectively?

*e* Leave the third portion of the sulphurous acid from *a* for several days exposed to the air in an open test-tube or bottle. Then add barium chloride and pure hydrochloric acid, and compare the result with that in *c*.

*f* To 2-3 c.c. of potassium dichromate solution, add three or four equivalents (a large excess) of dilute sulphuric acid. What substances does the mixture contain? Lead a stream of sulphur dioxide through the solution until no further change is observed (?).

*g* Take 2-3 c.c. of potassium permanganate solution, treat as in *f* (?), and answer the same questions (?).

*h* Fill a bottle with the gas by upward displacement, introduce some moistened litmus paper or grass, and a small piece of an apple, and close with a glass plate (?). Place another piece of an apple in an evaporating dish. Later, remove the first piece of apple from the bottle and place it on a

watch-glass. After exposure to the air for a day or more, compare the pieces of apple (?)

What properties of sulphurous acid are illustrated in *e*, *f*, *g*, and *h*, respectively?

### 90 Sulphites

*a* To 1 g of sodium sulphite add any dilute mineral acid (that is to say, one of the common acids, but not an organic acid such as acetic) (?) Formulate this action completely

*b* Dissolve a minute amount of sodium sulphite in water and add bromine-water in excess (test? The color must remain) Remove the excess of bromine by boiling. Add barium chloride solution (?) and then pure hydrochloric acid (?) Compare this experiment with that in 89 *d*, consider whether it is probably the molecular sodium sulphite, or the sulphite-ion, which is oxidized and make the equation accordingly (?)

*c* Heat persistently about 1 g of sodium sulphite in a porcelain crucible, supported on the clay triangle over a blast-lamp. When cool, acidify with hydrochloric acid (?) and note the odor. If any sulphur is precipitated, account for its formation.

*d* Place about 1 g of sodium bisulphite in a hard glass test-tube and heat cautiously with the tube in a horizontal position (why?) Note the odor (?) and whether any vapor condenses (?) This behavior is typical of that of many acid salts. What would be the final effect of heating sodium bisulphite more strongly and for a longer time? In what way is the behavior of potassium bisulphate different (87 *a*), and why?

### 91. Thiosulphates

*a* Dissolve about 5 g of sodium sulphite in about 20 c.c. of water in a small flask. Add 4-5 g of flowers of sulphur to the solution and boil gently over a small flame for 10-15 minutes. Filter off the clear solution and divide into two parts.

*b* To one portion add excess of any dilute mineral acid (?) Note the odor (?)

c Heat persistently about 1 g of sodium thiosulphate in a porcelain crucible over a blast-lamp (?). Note the appearance of the residue (?). When cold, add dilute hydrochloric acid (?) and identify the products. If any odor was observed during the heating, can you now account for it?

**92 Reduction of Sulphur Compounds** [Instructions] Mix a pinch of any salt of a sulphur acid with an equal amount of anhydrous sodium carbonate. Slightly char the end of a match from which the head has been removed, and rub the charred part, which should be about an inch in length, with a heated crystal of hydrated sodium carbonate. Moisten the above mixture with water, place some of it on the end of the match, and heat in the reducing region of a small Bunsen flame. Put the result on a clean silver coin lying in a watch-glass and moisten with one drop of water (?). Examine the coin (?). Then add some dilute mineral acid and note the odor (?). This, known as the "hepar" test, is a test for sulphur in any form of combination.

## CHAPTER XIV

### OXYGEN ACIDS OF THE HALOGENS

#### 93 Hypochlorous Acid from Bleaching Powder

*a* Take about 2 c c of bleaching powder\* with 20 c c of water in a test-tube, shake from time to time and finally filter to obtain a clear solution. Meanwhile arrange an apparatus (Fig 17, p 51), to generate carbon dioxide, using marble and hydrochloric acid. Pour most of the clear bleaching powder solution into another test-tube, and pass carbon dioxide through it for 5 minutes. What is the precipitate [R 310]? Filter again, to obtain a clear solution of hypochlorous acid for use in *c*.

*b* In the rest of the bleaching powder solution dip strips of litmus paper. Leave one in the solution (?). Does bleaching powder solution bleach? Hang the other in the air and examine later (?). What acid here liberates the hypochlorous acid? To what class of chemical actions does that on the litmus belong?

*c* In the hypochlorous acid solution from *a* place small pieces of (a) litmus paper, (b) paper with printing on it [R 398], (c) paper with writing in ink [R 634] and (d) in pencil [R 378], and (e) colored calico. Observe and record the effect on each (?). Which of these owe their color or blackness to free carbon, and which to colored organic compounds? Does hypochlorous acid oxidize free carbon? What does it oxidize?

*d* How could you prepare an aqueous solution of pure calcium hypochlorite [R 307-308]?

\* From a freshly opened "tin can" of the substance. When kept in a bottle it is likely to be decomposed by the carbon dioxide in the air.



94 Chlorine Water [Hood] Set up an apparatus to generate chlorine as in 48 *b* and use in 94 *a* and in 95 *a*

*a* Make 10 c c of an aqueous solution of chlorine in a test-tube. To the solution add a drop of indigo solution [R 311] (?)

*b* What evidence does experiment *a* furnish that hypochlorous acid is a more active oxidizing agent than is atmospheric oxygen? Why is it thus more active?

95 Chlorates [Hood]

*a* Dissolve 3 g (weighed on laboratory scales) of solid potassium hydroxide in 7 c c of water in a test-tube and saturate (Test? The solution must cease to feel soapy) the solution with chlorine. While the saturation is proceeding, calculate the volume of chlorine (at 0° and 760 mm) required to interact with 3 g of potassium hydroxide, one atomic weight of chlorine being needed for each molecule of potassium hydroxide. At five bubbles to 1 c c, how many bubbles of chlorine will be used? Observe how many bubbles issue from your apparatus in fifteen seconds, and calculate how long the operation may be expected to take (?) Crystals will appear during the process of saturation and will increase in quantity as the liquid afterwards cools. Filter off the crystals on a small filter paper, and examine the filtrate and the crystals (in *b*), separately, as follows

Add to the filtrate dilute nitric acid (this is to destroy potassium hydroxide, in case any remains—no equation needed), and test with a few drops of silver nitrate solution (?) What radical is shown by this test to be present (64 *a*)? What product is thus shown to have been formed by the interaction of chlorine and potassium hydroxide?

*b* Examine the crystals from *a* with a lens and describe them. Dry the crystals, heat them in a narrow tube, and test for oxygen (?) Dissolve the residue from this operation in distilled water and add silver nitrate solution (?) What substances constituted the crystals and the residue, respec-

tively? From the behavior of the former substance during making, what do you infer as to its solubility? Is the inference correct (Appendix IV)?

What effect was observed on adding silver nitrate solution to a solution of potassium chlorate (84 a)? How may the chlorate radical be distinguished from that of the chlorides? The crystals of potassium chlorate made in *a* are not free from traces of potassium chloride (why?), and could not therefore be utilized for this test. What method should you suggest for purifying the chlorate?

*c* To a minute amount of finely powdered potassium chlorate add two drops of pure, concentrated hydrochloric acid (?). The yellow substance is formed by decomposition of one of the products [R 314] (?). How would a chloride behave with hydrochloric acid?

Give the three ways of distinguishing chlorides from chlorates.

#### 96 Perchlorates

*a* Measure 600 c c of water into your 1-liter bottle, and mark the level reached. Observe the temperature and pressure of the air and calculate the weight of potassium chlorate which will be necessary to give 600 c c of oxygen under these conditions (the tension of aqueous vapor may be neglected, as the vapor will occupy only about 10 c c of the 600 c c at 18°) and at the same time leave the perchlorate and chloride as a residue. This stage is reached when one-fifth of the total oxygen has been evolved. In other words, take so much of the chlorate as, if completely decomposed, would furnish five times 600 c c.

Fill the 1-liter bottle with water and invert it in the pneumatic trough. Weigh the calculated amount of chlorate into a hard glass test-tube, which has previously been closely fitted with a one-hole cork and delivery tube, and see that the apparatus has been made air-tight. Gently heat the chlorate and collect in the 1-liter bottle enough oxygen to fill the bottle to

the mark, measured, of course, when the mark is at the same level as the water in the trough. Proceed slowly towards the end so as to allow the gas to cool, stop heating when the mark is reached, and remove the delivery tube at once from the water. Pour the melted substance into a mortar before it has time to solidify. Pulverize the mixture.

The mixture consists mainly of the chloride and perchlorate of potassium. The solubilities (grams of the salt dissolved by 100 c.c. of water) of these salts are as follows

	15°	20°	100°
Potassium chloride	33	35	56
Potassium perchlorate	1.5	1.8	20

To separate the substances, calculate approximately the amount of potassium chloride which must be present when one-fifth of the oxygen has been liberated



Shake the powder persistently with an amount of cold water just sufficient to dissolve this salt. Cut, fold, and place in a funnel a filter paper just large enough to hold the undissolved material. Collect the latter upon the filter and wash it with a few drops of cold water. Calculate the amount of water which at 100° will dissolve the residue, assuming it to be potassium perchlorate. Dissolve it in this amount of water by boiling, and allow the solution to stand for an hour or two. Collect the crystals upon a filter, wash them as before, and dry them.

b. Dissolve a little of the substance in distilled water and test with silver nitrate solution (?). Explain (64 d).

To a minute amount of the crystals add two drops of pure concentrated hydrochloric acid [R 315-316] (?). Why does the result differ from that when potassium chlorate was treated with the same acid (95 c)?

Place about 1 g. of the crystals in a narrow test-tube, heat, and test for oxygen (?).

How could you distinguish a perchlorate from a chloride, and from a chlorate?

### 97. Bromic and Iodic Acids

*a* Take two test-tubes and place in one a minute fragment of iodine and in the other 2-3 drops of bromine-water. Add about 5-10 c c of water and a little carbon disulphide to each, and shake (53 *a* and 57 *a*). The carbon disulphide is added simply for the purpose of collecting the halogen and making its presence obvious. Now pass chlorine (generated as in 53 *b*), a few bubbles at a time, through (or add chlorine-water, a few drops at a time, to) the water in the test-tubes, alternately, and shake vigorously after each addition of chlorine until a change is seen [R 318] (?). Which of the halogens is first affected, and why?

*b*. To about 10 c c of water in a test-tube add a single drop of potassium iodide solution and then a single drop of potassium bromide solution. Shake. Pour away three-fourths of the solution and add water. Introduce also a few drops of carbon disulphide. Now pass chlorine (generated as in 53 *b*), a few bubbles at a time, into the liquid, or add chlorine-water a little at a time, shaking vigorously after each addition of chlorine (?). Continue until no further changes occur, and explain all the changes which are observed. This procedure is used in analysis for recognizing a bromide in presence of an iodide.

*c* Prepare some dilute bromic acid by taking 2-3 c c of potassium bromate solution and adding an equal volume of dilute sulphuric acid (?). Make the equation for this double decomposition. Is the action complete (64 *d*)? In what follows, disregard the substances present with the bromic acid, and place the latter only in the equation. Drop into this solution a single small crystal of iodine and shake repeatedly, allowing the mixture to stand for some minutes after each shaking(?). Pour off the solution from any undissolved iodine, to

the clear liquid add a few drops of carbon disulphide, and shake (?) What free halogen is here detected? What does this show in regard to the relative tendencies of bromine and iodine to unite with oxygen?

What inference can you draw from *a* in regard to the relative activity of chlorine, as compared with bromine and iodine, towards oxygen? What would be the action of iodine upon a solution of chloric acid?

Which variety of chemical change was here observed? How could you show, by a single experiment, that, although no change is visible, the bromic acid actually is formed when the sulphuric acid is added, above, and that it is the bromic acid, and not the potassium bromate, which interacts with the iodine?

## CHAPTER XV

### THE ATMOSPHERE, NITROGEN, AMMONIA

**98 Preparation of Nitrogen from Air** Place a large plug of tightly rolled copper gauze, or of copper turnings held at each end by asbestos, in the center of a hard glass tube (Fig 11, p 24) Fit with corks and short glass tubes, and connect with the short tube of the aspirator (Fig 14, p 36) Fill completely with water the bottle and long tube of the aspirator and close the latter with a screw clamp [Stoiceroom] Arrange a vessel to catch the water discharged Now heat the copper red-hot and then partly open the clamp so as to allow the water to be syphoned off in a very slow stream The air will pass over the heated copper What change does the copper undergo, and what collects in the bottle? After three-fourths of the water has run out, close the clamp, disconnect the hard glass tube, attach a delivery tube in its place, elevate the end of the syphon, and replace the nozzle by a small funnel supported by a clamp Pour water into the funnel, and drive the gas over into a bottle of water inverted in the pneumatic trough Ascertain whether this gas supports combustion (?) Describe the gas as regards color and smell (?) What other gaseous substances, besides nitrogen, does this gas contain?

Other ways of removing oxygen from the air are described elsewhere (15, 99, and 105 d)

**99 Proportion (by Volume) of Oxygen in the Air** [Quant] (from Cooley's *Laboratory Studies*) Provide a large test-tube with a two-hole cork (a rubber stopper is apt to slip out in use) Into one hole fit a short piece of glass tubing terminating in a rounded nozzle, the tip of which projects but little beyond the

bottom of the stopper. Into the other hole fit a short glass rod. Test the apparatus for air-tightness. Connect the upper end of the glass tube with a short-stemmed funnel by means of a piece of rubber tubing (15 cm long) as in Fig 25, and support the funnel in a clamp.

Disconnect the test-tube, temporarily, and remove the glass rod from the cork. Prepare an alkaline solution of potassium pyrogallate by mixing 3 c.c. of pyrogallie acid solution with 20 c.c. of a solution of potassium hydroxide specially prepared for this experiment, and pour this into the funnel. The following operations should consume as little time as possible, as the alkaline solution gradually absorbs oxygen from the air of the room, and thereby becomes useless for further absorption. Now open the clamp and permit this solution to fill the rubber and glass tubes completely down

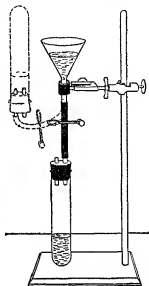


Fig 25

to the opening of the nozzle. Replace the test-tube, fitting the cork tightly into its mouth. Finally, reinsert the glass rod, and so inclose a volume of air equal to the content of the test-tube and at the temperature and pressure of the atmosphere.

Now open the clamp, taking care not to warm the test-tube by handling (use a piece of filter-paper when touching the test-tube). A few drops of the alkaline solution will enter the test-tube and, as the oxygen is absorbed, more of the solution will flow in. Close the clamp and invert the test-tube once or twice in order to bring the liquid thoroughly in contact with the inclosed air. Finally, while the test-tube is in the inverted

position, reopen the clamp and equalize the levels of the liquid in test-tube and funnel by raising or lowering the former. Then close the clamp, restore the test-tube to its original position, and mark the levels of the surface of the liquid and of the bottom of the cork by means of paper labels or rings cut from rubber tubing.

Disconnect the test-tube and wash out the liquid, taking care not to get the alkaline solution upon the hands. Then, by means of a burette, or graduated cylinder, filled with water, measure the volumes required to fill the test-tube up to the lower and upper marks respectively (?). The former is the volume of the oxygen, the latter that of the air. Calculate the percentage of oxygen in the air by volume (?).

#### 100. Other Components and Density of Air

*a* Place 2–3 c c of clear barium hydroxide solution in the bottom of a small beaker and leave it exposed to the air for some hours (?).

*b* Blow air from the lungs through a glass tube into 2–4 c c of clear barium hydroxide solution (?). Explain (?).

*c* How may the presence of aqueous vapor in air be demonstrated (43 *b*)? How may its quantity be measured?

*d* The weight of a measured volume of air, or of nitrogen, may be determined by the method described in 124. From the data so obtained the density may be calculated.

#### 101. Nitrogen

*a* Place about 10 g of pure sodium nitrite and about 8 g of ammonium chloride in a 250 c c flask fitted with safety and delivery tubes (Fig 10, p 22). If *b* is to be performed, insert between the flask and the delivery tube a U-tube containing calcium chloride for drying the gas.

Clamp the flask by the neck to a ring-stand, add about 15 c c of water, and warm gently [CAUTION!]. As soon as the action begins, remove the flame, bring a dish of cold water under the



flask, and cool it for a few seconds at a time so that the action may not become too violent, but may run uniformly. After sufficient time has been allowed for the displacement of air from the apparatus, fill a bottle with the gas over water in a pneumatic trough. Has the gas odor or color? Does it support combustion?

*b* (Two students working together) In a piece of hard glass tubing, fitted with corks and short pieces of glass tubing, place a porcelain boat half filled with powdered magnesium. Connect one end of this tube to the outlet tube of the flask in a generating nitrogen. Heat the magnesium strongly (two Bunsen burners may be necessary). What action is noticed? What is the color of the product? Transfer the contents, when cold, to a dry test-tube, close with a cork, and use in 102 *b*. May the same product be formed when magnesium is heated in the air? What other compound would be formed under the latter conditions? Examine the glass tube and name the shining black substance on the inside surface [R 425] (?)

#### 102 Ammonia

*a* Fit a small flask with a cork and L-shaped exit tube, and connect the latter with a U-tube. Put a little water in the bend of the latter so as just to close the passage. Test the apparatus for air-tightness. Place in the flask a mixture of powdered quicklime and ammonium chloride, about 10 g of each, and warm gently [Hood]. After the air has been displaced, the whole of the gas should dissolve in the water. Use this solution of ammonium hydroxide in 103.

\* If required to determine the density of ammonia, which of the various methods should you select (31 *a*, 84, or 124)?

*b* To the product from 101 *b* add a little water, boil, and note the odor (?). What other substances would behave in the same way as magnesium nitride?

*c* Heat a small piece of gelatine in a dry test-tube and note the odor (?).

### 103 Ammonium Hydroxide. An Inactive Base: Salts of Ammonium

*a* Test the reaction towards litmus paper of the solution made in 102 *a* (?) What substance is present? Hold a glass rod dipped in concentrated hydrochloric acid over the solution (?) What substance is shown by this test to be present? Formulate the relations (in equilibrium) of all the substances in the solution

*b* Expose 1-2 c c of the solution from 102 *a* in an evaporating-dish for 24 hours and then note the odor (?) and test with litmus (?) Heat [Hoon] another small portion in an evaporating-dish for some minutes, and note the odor from time to time (?) Does the aqueous solution of this gas behave like that of hydrochloric acid, or like that of hydrogen sulphide? What other gases resemble ammonia in this respect?

*c* Neutralize (test ?) the remainder of the solution from 102 *a* with dilute sulphuric acid and evaporate to dryness on a water bath (?) Formulate this action after the model in 69 *a* (second par), and explain what happens during neutralization to each of the substances present in the ammonium hydroxide solution (?)



Fig 26

Scrape the residue into the middle of the dish, invert over it a funnel smaller than the dish, the stem of which has been closed with a paper plug, and heat the center of the dish strongly and persistently with a small flame (Fig 26) (?) To learn whether the sublimate is identical with the residue, examine it for the ammonium radical (103 *d*, below), and the sulphate (86 *b*) radical

*d* Dilute 1-2 c c of ammonium chloride solution and add to it 1-2 c c of sodium hydroxide solution (?) Note the odor (?) Formulate, study, and explain this action according to the directions in 69 *a* (second par) Include in the formulation the liberation of the ammonia. What is an inactive base?

*e* The evolution of ammonia when an active base is added to a solution of any ammonium salt is used as a test for the latter. Why would not simply heating the salt by itself (as in 103 *c* and *f*) serve as a test? What salt of ammonium that we have used gives, when heated, no ammonia? Name other salts of ammonium which likewise give no ammonia [R 357, 603] (?) Conversely, what substance when heated gave ammonia, yet contained no ammonium salt (102 *c*)? What other substances behave thus [R 340, 422]?

*f* Place some ammonium chloride in the middle of an open, hard glass tube. Support this in a very slightly inclined ( $5^\circ$ ) position by means of a clamp attached close to one end. Put pieces of moistened litmus paper (both colors) in each end, and heat the salt strongly (?). Watch closely the effect on the papers at each end (?). What does this experiment show to be the action of heat on ammonium chloride? Which gas appeared first at the ends of the tube, and why first at both lower and higher ends? What should be the relative speeds, by calculation, of the two gases [R 78]? Why does the second gas reach the ends so very much later than one might expect? Has gravity an influence on any of these results?

## CHAPTER XVI

### OXIDES AND OXYGEN ACIDS OF NITROGEN

#### 104 Preparation of Nitric Acid [Hood]

*a* Pulverize about 15 g of sodium nitrate and place it in a dry retort or distilling-flask [Store:room] Cover the salt with concentrated sulphuric acid and wait until this liquid has permeated and moistened the entire mass Support the vessel by a clamp upon a sand bath and allow the neck of the retort (or side-tube of the flask) to extend to the bottom of a small flask (the receiver, Fig 27) In order that the vapor of the nitric

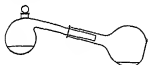


Fig 27

acid may condense, this flask is immersed in a vessel of cold water, and is covered with filter paper which is continually moistened Heat the retort gently until a sufficient amount of nitric acid has been obtained, and preserve the product in a corked test-tube for use in *b* [CAUTION! Serious wounds may be caused by allowing this liquid to come in contact with the skin] What is the composition of "concentrated" nitric acid [R 348], and how does the acid here made differ from the "concentrated" acid? What law teaches us to expect that the acid here prepared will be more active (and dangerous to handle) than the "concentrated" acid?

*b* Note the color of the acid prepared in *a* (?) Blow some air from the blast through the acid (?) What is the color of pure nitric acid? To what substance was the color of this sample due, and by what action was it formed? What property of nitric acid does its formation indicate? Blow the moist air

of the breath over this specimen (?) What property does this indicate? Determine the boiling-point of anhydrous nitric acid by boiling this sample in a distilling-flask [Stoiceroom] with a thermometer immersed in the vapor (?)

#### 106 Nitric Oxide

*a* Into a small flask, fitted as in Fig 10 (p 22) and containing about 10 g of copper, pour 10 c c of water and then an equal amount of concentrated nitric acid. Collect the gas over water in the pneumatic trough. Note the color of the gases first formed, and observe the color of the pure gas finally collected over the water. Fill two bottles (for *b*, *c*) and the large test-tube (for *d*) with the gas.

The production of colored gases, when copper is added, is used as a test for nitric acid.

*b* Into one bottle introduce a burning match (?) Note also the effect of opening this bottle to the air (?) This effect may be used as a test for nitric oxide, or, conversely, for oxygen. How should you apply it for each of these purposes?

*c* Into the second bottle lower a deflagrating spoon with a very little vigorously burning, red phosphorus (?) What change in volume does the gas undergo in this action?

*d* Transfer without loss the nitric oxide in the test-tube to a small beaker filled with water and inverted in the pneumatic trough. Prepare some oxygen by placing 1 g of sodium peroxide in a side-neck test-tube (Fig 28) and introducing water, drop by drop, from the dropper. Fill the test-tube with oxygen and add this to the nitric oxide (?), thus securing equal volumes of the gases. Shake the beaker, keeping the mouth well immersed, until no further change occurs. Transfer the remaining gas, which must be either nitric oxide or oxygen, back to the test-tube. Note its volume, and determine what gas it is (?)



Fig 28

What relative volumes are (a) used for the interaction and (b) required by the equation?

How might the proportion of oxygen in the air be determined by application of this interaction?

*e* Prepare 10 c.c. of a concentrated solution of ferrous-ammonium sulphate [Note 38, p. 87] (or ferrous sulphate) and divide into three portions. Into one pass a gentle stream of nitric oxide (?). Boil the liquid (?).

*f* Add to the second portion of ferrous-ammonium sulphate solution an equivalent amount of dilute sulphuric acid, heat to boiling, and add nitric acid drop by drop (mix after each drop) until there is no further action (?). What gas is liberated?

*g* Dissolve a single crystal of sodium nitrate in 1-2 c.c. of water, and add a part of this solution to the remainder of the ferrous-ammonium sulphate solution from *e*. Pour concentrated sulphuric acid cautiously and steadily down the side of the test-tube until it forms a considerable layer at the bottom of the tube. Note the brown ring between the layers, and explain by reference to *e* and *f* [R 350] (?). This constitutes a delicate test for nitric acid or a nitrate. In what way does the avoidance of mixing (and consequent ring-formation) contribute to the delicateness of the test?

*h* Take 2-3 c.c. of concentrated nitric acid in a test-tube, warm it slightly, and lead through it a stream of nitric oxide (?). By waiting until the air has been wholly displaced, make certain whether the colored gas is formed by an interaction of the nitric oxide with the nitric acid, or simply by contact with the air in the test-tube (?). To observe the color of a gas, do not look across the test-tube, but down the tube at a sheet of white paper.

#### 106 Nitrogen Tetroxide

*a* Fit a hard glass test-tube with a cork and L-shaped exit tube, and see that it is air-tight. Place 8-10 g. of lead nitrate in the tube and clamp it in a horizontal position. Tap the tube

until the salt settles in a layer, leaving a wide channel above it. Prepare a strong solution of sodium hydroxide by dissolving 2 g. of the solid in 7 c.c. of water and allow the delivery tube to reach the bottom of this solution. Now heat the lead nitrate (?) persistently until gas is no longer given off, or until the liquid is no longer soapy to the touch. If all the gas is not absorbed in the alkali, test the escaping bubbles for oxygen (?). Label the solution and set it aside for use in 111 *d*.

*b* What is the residue? What other nitrate have we decomposed in the same way (22)? This behavior when heated is typical of the nitrates of the heavy metals, and may be used for identifying them. Which nitrates, when heated, would leave the metal, instead of the oxide [R 60]? Why do commercial specimens of mercuric oxide [R 534], when heated in the preparation of oxygen, frequently give off a brown gas?

#### 107 Principles Involved in Making Nitric Acid

*a* Addition of copper (105 *a*) to a liquid containing nitric acid gives red vapors. Is this a test for any substance containing the nitrate radical, or only for nitric acid? To answer this question dissolve a little sodium nitrate in water, add copper and warm (?).

*b* Was nitric acid formed in 104 on mixing sodium nitrate and sulphuric acid, before the distillation began? Solve this question by mixing sodium nitrate (finely pulverized) with concentrated sulphuric acid, adding a very little water [CAUTION] and agitating for a minute or so. Lower a glass rod dipped in ammonium hydroxide solution into the test-tube (?). Apply also the copper test as in *a* (?).

*c* Is the action of sulphuric acid upon sodium nitrate reversible? Take 2-3 c.c. of saturated sodium-hydrogen sulphate solution and add to it an equal or even greater volume of pure concentrated nitric acid. Cool the mixture in a stream of cold water and stir with a glass rod (?). The salt solution must be sufficiently concentrated, otherwise the experiment will fail.

Examine with a lens the crystalline product that separates out (?) If the action is reversible, what enabled us to obtain a large yield of nitric acid in 104?

d Will other acids behave like sulphuric acid? Mix some pulverized sodium nitrate with phosphoric acid, agitate for a minute or two, and apply the copper test as in a (?) Could phosphoric acid be used in the preparation of nitric acid as in 104? Why? Could hydrochloric acid be used [R 145, 348, 356]? Could hydrofluoric acid be used [R 206, 348]? Give reasons for your answers (?)

#### 108 Properties of Nitric Acid

a Test dilute nitric acid with litmus paper (?)

b Add 1 g of sulphur to 2-3 c.c. of concentrated nitric acid and boil [Hood] for two or three minutes (?) Is there any evidence of action? Pour the clear liquid into another test-tube, dilute with water, and test for the sulphate radical (?) What property of nitric acid is here shown?

c The interaction of dilute (16 c) and of concentrated (16 d) sulphuric acid with metals has already been studied. Try the action of (a) magnesium and (b) zinc, separately, either upon dilute or upon concentrated nitric acid, and of (c) copper upon both, and explore the whole action thoroughly in each of the four cases as follows

Fit up a side-neck test-tube with a dropping-funnel passing through a perforated cork, and attach a delivery tube (or use an ordinary test-tube with cork and delivery tube). Place a small amount of the metal in the tube and admit the acid from the dropping-funnel. After the air has been displaced, collect the gas over water in a test-tube inverted in the pneumatic trough (or in an evaporating-dish)

If the gases in the generating tube remain colored, nitrogen tetroxide is present. If the gas is at first colored, but becomes colorless, nitric oxide is present. Confirm by admitting air to the tube in which it has been collected (To see color, look down



the tube) (?) Hydrogen, if heated alone, would show neither of these properties, but might be identified by its inflammability (?) If both hydrogen and nitric oxide are heated, why may we not feel confident of being able to cause the former to burn when thus diluted? How can the nitric oxide be separated (105 *d* or *e*) so as to leave the hydrogen in an inflammable condition? Examine the gas in each case for these three substances.

If ammonia is formed in any of these four cases by complete reduction of the nitric acid, where will it be found, and in what condition? (Consider all the circumstances carefully, or you will answer wrongly.) Test for its presence (103 *d*) (?)

Evaporate on a water bath [Hood] the solution remaining in the side-neck test-tube after any one of these experiments (?) Collect the residue and heat it in a dry test-tube (?) In what form of combination was the metal (106)?

*d* Grasp a test-tube by means of a strip of folded paper (Fig 8, p 16), place in it a piece of granulated tin, and add some concentrated nitric acid (?) When the action has exhausted itself, add much water and boil. Fit a small filter paper carefully into a funnel [Note 24, p 10], collect the solid product upon the filter and wash [Note 39, below] precipitate and paper with water. Test the filtrate as it runs through to see whether it becomes neutral (?) Inference? Spread the filter paper with the precipitate upon a water bath or radiator to dry and ascertain as in 106 *a* whether the product is a nitrate (?) Why would the test in 105 *g* be unsuitable here?

*e* Comparing dilute and concentrated nitric acid with the same forms of sulphuric acid, what points of resemblance and of difference have you observed?

Account for the differences in the actions of dilute and of concentrated nitric acid in *c*, *d*, and *e*, in respect to the gaseous product of reduction which is typical of each.

*f* Dip a piece of wool in concentrated nitric acid, or note the nature of the products formed when the acid falls upon

the hands or clothing (?) Would cotton behave in the same way? Explain [R 350] Moisten the stained wool with ammonium hydroxide (?)

*g* To 1-2 c c of nitric acid add 3-4 c c of pure, concentrated hydrochloric acid, warm gently, and note the appearance and odor (?) Will these acids, singly, attack all metals? Explain (?) What metals are attacked only by the mixture (*aquo regia*), and why? What form of combination do the metals assume?

*Note 39* — In filtering, observe the directions in Note 24, (p 10) To wash a precipitate first let the mother liquor drain away completely and press the precipitate with a spatula Then cover the contents of the funnel, including the whole paper (why?), completely (and repeatedly, if necessary) with the washing material When the washing is complete, dry the product by pressing with dry filter paper

#### 109 Nitrous Oxide

*a* In a test-tube or small flask provided with a cork and delivery tube (Fig 16, p 46), place 10 g of ammonium nitrate Heat cautiously with a small flame [CARE!] and, after the air has been expelled, collect the gas in two bottles over water (warm water, if available Why?) Why does the gas collect so slowly, relatively to the vigor of the action? What are the relative volumes of the products at 100°?

*b* Into one bottle lower a glowing splinter of wood (?)

*c* Into the other bottle lower a deflagrating spoon containing a very little burning, red phosphorus (?) If this experiment were to be conducted in a closed vessel, what, if any, change in pressure would be observed after the products had cooled?

#### 110 Nitrates

*a* How does lead nitrate behave when heated? What other nitrates behave like it? How does ammonium nitrate behave when heated?

*b* Take 2-3 g of sodium nitrate in a hard glass test-tube,

and heat strongly and persistently with the blast lamp until the evolution of gas ceases. Test the escaping gas for oxygen. Use the residue in 111 *a*. What nitrates behave in this way when heated?

#### 111. Nitrites and Nitrous Acid.

*a* When the residue from 110 *b* has cooled, add not more than 3 c.c. of water, shake vigorously until the whole has dissolved, and divide into three parts. To one portion add dilute sulphuric acid (?). How could a nitrite be distinguished from a nitrate?

*b* To 5 c.c. of starch emulsion add a drop of potassium iodide solution and some dilute sulphuric acid, and then introduce a little of the solution from *a* (?).

*c* Dilute 1-2 c.c. potassium permanganate solution with a large excess of dilute sulphuric acid, and add a drop of this mixture to the solution from *a* (?). The actions in *a*, *b*, and *c* serve for the detection of nitrites and nitrous acid. What other characteristic property of nitrites has been encountered (101 *a*)?

*d* Examine now the solution obtained by leading nitrogen tetroxide into sodium hydroxide (106 *a*). Take a portion of the solution and acidify (test?) with dilute sulphuric acid (?). To the mixture add a drop of diluted potassium permanganate solution (?) or some starch emulsion containing a drop of potassium iodide (?). What substance was present?

To ascertain whether this alkaline solution contains a nitrate as well as a nitrite, the latter must first be eliminated. To the remainder of the alkaline solution, transferred to a small flask, add at least 5 g. of ammonium chloride [Hoon] and heat to boiling (?). Explain the evolution of ammonia (?). What other gas is given off (101 *a*)? When the action is entirely over, add about 10 c.c. of water, and shake. Prepare 2-3 c.c. of a concentrated solution of ferrous-ammonium sulphate [Note 38, p. 87] (or of ferrous sulphate), add to it 1-2 c.c. of the solution to be examined, and complete the test for a nitrate described in

105 g (?) Write now the equation for the action of nitrogen tetroxide on sodium hydroxide

112 **Active (Nascent) State of Hydrogen** Dilute two drops of potassium permanganate solution with much water, and add an equal volume of dilute sulphuric acid to it. Divide into two parts. Through one pass a stream of hydrogen gas from a generator, or from the laboratory supply, or from a Kipp's apparatus (?). To the second add some zinc dust, and shake (?). Interpret the result [R 360] (?)

113 **Identifying an Unknown Substance I** Obtain [Instructor] a single, unknown solid substance. It will contain one of the following radicals

ammonium	sulphite	perchlorate
chloride	bisulphite	nitrate
bromide	sulphate	nitrite
iodide	bisulphate	hydroxyl (base)
peroxide	thiosulphate	
sulphide	chlorate	

The positive radicals will be limited to  $\text{NH}_4$ , Na, K, and Ca, of which only the first is to be identified. Record at the time the result of each observation. Record negative results also.

*a External Examination* Record the state (?), crystalline form (?), color (?), and odor (?).

*b Solubility and Reaction of Solution* Use a few particles to find out if it is soluble in water (?). If in doubt, proceed as in 38 a. Test also with litmus papers (?).

*c Effect of Heating* Heat 0.5 g in a dry test-tube. Does it melt (?), or otherwise change (?), and does it give off gas or vapor? Note the odor (?).

If WATER VAPOR is given off and condenses (?), the substance may be a hydrate, acid salt, or calcium hydroxide. Incline the mouth of the tube downwards, drive all the water off, dry out the tube with filter paper, and continue heating. Does it now change (?) or give off gas or vapor?

If a SOLID SUBLIMATE appears (?), what is it? Note the odor (?) and apply the test for the positive radical (?)

A COLORLESS GAS with an ODOR (?) may be ammonia or sulphur dioxide (?)

A COLORLESS, ODORLESS GAS may be oxygen (test?) Which three of the above radicals will give oxygen? What substance will remain, in each case, when all the oxygen has been driven off? Keep the tube and residue for use in *e*

A COLORED GAS may be nitrogen tetroxide (?) Inference?

*d Action of Concentrated Sulphuric Acid* To 0.5 g of the substance add two or three drops (not more) of concentrated sulphuric acid (?) If a pale yellow gas appears [CAUTION!] do not heat, as the gas (?) is explosive If no gas appears, warm gently (?)

A COLORLESS GAS (bubbling) which FUMES in the breath (?) Two possible sources (?)

A COLORLESS GAS, NON-FUMING, with an ODOR may be hydrogen sulphide or sulphur dioxide One possible source of former (?) and three of latter (?)

A COLORLESS GAS, NON-FUMING, ODORLESS may be oxygen (?)

A COLORED GAS may be vapor of iodine or of bromine (?) It may be nitrogen trioxide (?) If yellow, it is chlorine dioxide (?) Inference as to radical (?)

No GAS (no bubbling) indicates a sulphate or a base (?)

*e* To the residue from *c*, par 5, add two or three drops of concentrated sulphuric acid (?) What is the inference if the gas is brown (?) and if it is colorless, but fumes in the breath?

*f Conclusion* In some cases the foregoing experiments fail to distinguish between two possible radicals Apply special tests in these cases In each case, if a special test exists, confirm your conclusion by applying it

*g Report* State your conclusion, with reasons therefor (?)

*h* Obtain a second unknown, and proceed as before (?)

## CHAPTER XVII

### PHOSPHORUS

#### 114 Phosphine [Hood]

*a* Place a very small piece of calcium phosphide in a little water in a beaker (?). Try the reaction of the gas (not the liquid) with moist litmus papers (?). What mode of forming ammonia is similar to this, and how is it similar?

*b* Repeat, using dilute hydrochloric acid instead of water (?). What mode of forming hydrogen sulphide is similar to this, and how is it similar? In what ways does phosphine differ from ammonia [R 366]? Which of the differences are shown in these experiments? Why should we expect ammonia and phosphine to be alike? Test with litmus the water in which the calcium phosphide was placed (?), and explain.

#### 115 Metaphosphoric Acid

*a* Throw 2 g of phosphorus pentoxide, in minute portions at a time, into a beaker containing 10 c c of cold distilled water (?). Allow the liquid to stand for a few minutes, or until clear. Test the liquid with litmus paper (?). What acid is present [R 368]? Use the solution for *b* and *c* and 116 *a*. Why could not the product made by burning phosphorus in a closed volume of air be used in this case?

*b* To a part of the solution from *a* add silver nitrate solution, a little at a time, shaking between additions, until a permanent precipitate (color?) is formed (?). Is an action like this reversible? Is this action incomplete? To answer, add diluted (1 : 4 Aq) ammonium hydroxide solution, one drop at a time, observe whether the precipitate increases, and explain.

The first action of *b* is a reaction of what ion? What other substances would give it?

c. To 1 c c of albumin solution, add one or two drops of the solution from *a* [R 372] (?) This is a reaction of the free acid only, and not of metaphosphate-ion

#### 116 Orthophosphoric Acid

a Dilute the remainder of the solution of metaphosphoric acid from 115 *a* with 10 c c of water. Fit a small flask with a one-hole rubber stopper (or perforated cork), and insert a long piece of glass tubing, to act as a condenser. Boil the solution in this flask gently for an hour or more. If necessary, add more water to make up for the loss by evaporation. Cool the solution, treat portions of it with silver nitrate and with albumin, as in 115 *b* and *c*, and answer the same questions. How may the formation of this acid, during the boiling, be hastened [R 368]?

Like all double decompositions, the one with silver nitrate is reversible, and is therefore incomplete. Name the interacting substances in the reverse action (?) To stop this reverse action, destroy the acid by adding ammonium hydroxide solution one drop at a time, noting the effect, shaking, and examining again. What evidence is there that the action now goes further forward?

Finally, add concentrated nitric acid (?) Which way does the action now go?

b Heat 1 g of red phosphorus with 5 c c of dilute nitric acid in a test-tube (?) When the action has ceased, filter, if necessary, and drive off the water and excess of nitric acid completely by evaporation [Hoon] on a water bath. Mix with a few drops of concentrated nitric acid the syrup which remains, and evaporate once more. It is essential that all the nitric acid be finally removed (why?) Redissolve the syrup in water and test with litmus paper (?)

Treat part of the solution with silver nitrate as in 115 *b*, and answer the same questions (a black precipitate with silver

nitrate is metallic silver, due to reduction by phosphorous acid [R 373] formed by incomplete oxidation)

c Place in a test-tube 5 c.c. of the solution of ammonium molybdate in nitric acid, add to it two drops (only) of the solution of orthophosphoric acid prepared in *b*, and warm gently (?) This is a very delicate test for phosphoric acid, or orthophosphate-ion

#### 117 Phosphates

a Take some sodium phosphate (secondary sodium orthophosphate) solution and test it with litmus paper (?) What ions are present? Are acid salts always acid towards litmus? If not, explain why they are not Explain also the actual reaction of this solution

b To a very small part of the sodium phosphate solution add silver nitrate solution until the precipitation is complete (?) What is the precipitate (see 116 *a* and *b*)? To confirm this conclusion, test the reactions towards litmus of the sodium phosphate (*a*), and silver nitrate solutions singly? Test the mixture with litmus paper (?) What ion is evidently formed, and what product is therefore present?

c Prepare a little "magnesia mixture" by adding to 1 c.c. of magnesium sulphate solution a few drops of ammonium hydroxide and then excess of ammonium chloride solution Add to the rest of the sodium phosphate solution a little of this mixture (?) Scrape the walls of the test-tube, beneath the liquid, with a glass rod (?) In making the equation, disregard the ammonium chloride, which is added only to prevent precipitation of magnesium hydroxide This is another test for the presence of what ions?

d Strongly heat [Blast-lamp] 2 g. of dry sodium phosphate in an open crucible for twenty minutes, or until no further change is observed (?) Dissolve the cold mass in water (it dissolves very slowly), and test a portion of the solution with silver nitrate solution (?) This is a reaction of what ion?



Take the remainder of the solution, liberate the acid (?) by adding acetic acid, and introduce a few drops of the liquid into a solution of albumin (?)

Make a table showing the effects of the three phosphoric acids upon albumin and the colors of their silver salts. How could you identify salts of the three acids?

*e* Heat strongly [Blast-lamp] 2 g of microcosmic salt as in *d*. Note the odor (?) and reaction towards moistened litmus paper (?) of the vapors given off. Dissolve the residue in cold water and use the tests tabulated in *d* to learn what salt has been formed.

*f* Make a bead on a straight platinum wire as in 2 *c*, using microcosmic salt instead of borax. Of what must the bead consist? Now fuse with it (2 *d*) a minute particle of cupric oxide (?)

What difference do your experiments show as to the relative stabilities of  $\text{NaPO}_3$ ,  $\text{NaNO}_3$  (110 *b*), and  $\text{KClO}_3$ ?

### 118 Halides of Phosphorus

*a* What were the actions of water on the tribromide (54 *b*) and tri-iodide (58 *b*) of phosphorus?

*b* Place 2-3 c c of phosphorus trichloride in a dry test-tube and blow the breath over the tube (?). Add water drop by drop (?) until about 5 c c has been used, then boil the solution (Fig 8, p 16). Test the vapor with litmus paper (?) and with a rod dipped in ammonium hydroxide (?). Evaporate [Hoop] the solution to a syrup on the water bath (?)

*c* Transfer part of the syrup from *b* to a small test-tube and heat until the gas evolved may be ignited at the mouth of the tube (?). Note the odor of this gas before igniting it (?). Continue heating until the action is over. Ascertain according to 117 *d* which of the phosphoric acids constitutes the residue (?)

*d* Dilute 1 c c of potassium iodide solution with water and dissolve in the liquid a crystal of iodine. Add to this solution a little of the syrup from *b*, and shake (?)

*e* Place upon a watch-glass 5 or 6 small granules of phosphorus pentachloride and blow the breath over them (?) Throw them into 2-3 c c of water in a test-tube (?) and boil Test the solution with litmus (?) To a very small part of the cold solution add excess (test?) of silver nitrate solution (?) Filter What remains upon the paper (?) To the filtrate add diluted (1 4 Aq ) ammonium hydroxide one drop at a time (shake between drops) (?)

## CHAPTER XVIII

### OXIDES OF CARBON    HYDROCARBONS

#### 119 Carbon Dioxide by Oxidation

*a* Fit a hard glass test-tube with a cork and L-tube. Mix intimately in the mortar 2 g of pulverized cupric oxide with 0.5 g of pulverized wood charcoal and place in the tube. Clamp the test-tube in a horizontal position, and let the L-tube reach to the bottom of a test-tube containing limewater. Heat the powder persistently [Blast-lamp] and let the gases pass through the limewater (?). Examine the residue by rubbing vigorously under water in the mortar and washing away the lighter particles (?). What property of carbon is here illustrated? What important industrial processes depend upon this sort of reaction?

*b* Mix 2 g of litharge and 2 g of charcoal, and test as in *a*, using, however, only a Bunsen burner for heating (?). Answer the same questions (?).

#### 120 Carbon Dioxide, Preparation

*a* Place a few small pieces of magnesite (magnesium carbonate) in a hard glass test-tube fitted with a cork and L-tube and heat strongly. Pass the gas through 5 c.c. of limewater in a test-tube (?). What is the residue [R. 525]?

*b* Fit up a generating-flask (Fig. 10, p. 22) and connect with two wash-bottles (Fig. 23, p. 89) containing water and concentrated sulphuric acid, respectively (what is the use of each of these? The latter is unnecessary if 122 is omitted). Place in the flask some pieces of marble and pour upon them diluted hydrochloric acid. Collect the gas in three bottles by upward displacement of air, and cover them with glass plates.

What substances could be substituted for marble in this experiment? What other sources of carbon dioxide have been encountered (14 c, 119, 120 a, see also 123 a and c, 125 b, 126 b, 131 b)?

#### 121 Carbon Dioxide, Properties

a To one bottle add a little water, close tightly with the hand, and shake (?). Is the gas soluble in water, or not?

Use the second bottle to compare the weight of the gas with that of air. Employ baryta-water as a test.

b Set an empty bottle (filled with air) over the remaining full one, and mouth to mouth with it, and withdraw the plate. After ten minutes, replace the glass plate between the bottles, remove the upper bottle, along with the plate, and set it upright upon the table. Slip the plate aside for a moment, add some lime-water, replace the plate, and shake (?). Did the greater density of the carbon dioxide prevent its diffusing into, and displacing a part of the air? What are the relative rates of diffusion of air and carbon dioxide?

c Take two test-tubes containing distilled water, pass a current of the gas into one, to saturation, and test each with litmus paper (?). Boil the solution, and test again with litmus (?). Explain.

d Lead the gas into a little sodium hydroxide solution in a test-tube until the solution is saturated (test? Note 37, p. 86). Let the solution stand until it dries spontaneously (first residue). Heat the dry residue (?) in a test-tube, and determine what two things are given off.

To this residue after heating (second residue) add dilute hydrochloric acid until all action (?) ceases. Evaporate the solution on the water bath, and examine and taste this final residue (?). Having recognized the products of the last action, and taking into account the preceding observations, state what the nature of the second and first residues must have been (?). Write equations for all actions (?).

**122 Molecular Weight of Carbon Dioxide [Quant]**

Determine the weight of a measured volume of the gas by the method used for sulphur dioxide (84), and calculate the weight of the gram-molecular volume (?) What further information must we have to enable us to determine the formula?

**123 Carbon Monoxide [Hoop]**

*a* Heat about 10 g of oxalic acid crystals with concentrated sulphuric acid in a generating-flask (Fig 10, p 22), and fill a bottle over water with the gas which is given off. Shake with limewater (?). With what substance should we wash the gas to remove the carbon dioxide? Arrange a wash-bottle to purify the gas. Fill two bottles with the purified gas over water. Test one with limewater again (?). If the gas is pure, burn that in the other bottle, add limewater at once, close quickly, and shake (?).

*b* Devise a way of ascertaining roughly the relative volumes of the two gases generated in *a*, and measure the proportion in a test-tube full of the mixed gases.

*c* Pass a stream of the purified carbon monoxide over a little pulverized cupric oxide, heated in a boat in a hard glass tube (?). What gas is formed? What remains in the boat? What is here the reducing agent?

**124 Molecular Weight of Carbon Monoxide [Quant]** Obtain [Store-room] a round-bottomed, 250 cc flask. Fit it with a rubber stopper through which passes a short, straight tube. Attach to the latter a short piece of rubber tubing closed with a strong pinch clamp. Make a mark on the neck at the bottom of the stopper, so as to be able to measure the exact content of the flask up to the stopper. Place 30 cc of water in the flask, insert the stopper, remove the clamp, and boil the water with a small flame for about five minutes, so as to drive out all the air. Close the rubber tube with the clamp and remove the flame quickly, wipe the flask and allow it to cool. When it has assumed the temperature of the air, weigh

the whole carefully, suspending the flask on the balance by a thread tied round the neck (?). Connect with the apparatus delivering pure carbon monoxide, and open the clamp a very little so as to admit a slow stream of the gas. When the flask is full, close the clamp, disconnect from the generating apparatus, open the clamp for an instant to restore the pressure to that of the atmosphere, and weigh again (?). The gain in weight represents the weight of the carbon monoxide. Read the barometer and thermometer (?). Subtract from the barometric reading the aqueous tension at the observed temperature. Ascertain the volume of the flask by filling with water to the mark from the graduated cylinder.

Calculate the weight of the G M V of the gas (?).

To what class of gases would this method of determining the density and molecular weight be applicable? Why could not this method be used for carbon dioxide?

#### 125 Methane (Marsh Gas)

a Pulverize about 5 g of fused sodium acetate and about 20 g of soda-lime (a mixture of quicklime and sodium hydroxide). Mix the ingredients intimately in the mortar, and place in a large test-tube fitted with a one-hole cork and delivery tube (Fig 9, p 17). Rap the test-tube gently so as to form a space for the passage of the gas. Then clamp the tube close to the cork in a slightly inclined ( $5^\circ$ ) position, so that it slopes toward the mouth (why?). Slip over the tube a cylinder of wire gauze, and, beginning at the rear or sealed end, heat the contents gently until the evolution of gas is uniform. When all the air is displaced, collect one bottle of gas over water.

Attach a small nozzle to the end of the delivery tube and ignite the gas. Note the color and degree of luminosity of the flame (?). Hold over the jet a dry inverted beaker and observe one product of the combustion (?).

b Hold the bottle containing the gas mouth downward and apply a light (?). Quickly pour into the bottle some lime-

water, and shake (?) What volume of oxygen is required for the complete combustion of one volume of methane, and what ratio will the resulting volume of gases bear to the original volume of methane, at  $0^{\circ}$  and at  $100^{\circ}$ , respectively?

126 Ethylene [Hood]

a Fit a 250 c c flask with a doubly-bored cork, through which pass a dropping-funnel and L-tube. Attach a gas-washing bottle containing a little water, and connect an L-shaped delivery tube. Test the apparatus to see that it is air-tight. Place in the flask about 20 g of phosphorus pentoxide, and clamp it to a ring-stand over a sand bath. Introduce into the bulb of the dropping-funnel (or substitute, 36 b) some alcohol. Finally, heat the phosphoric anhydride, and admit the alcohol drop by drop.

b Fill a bottle with the gas over water and apply a light (?). Quickly pour some limewater into the bottle, and shake (?). Attach a nozzle to the exit tube of the washing bottle and raise the other tube clear of the water in the washing-bottle (why?), ignite the gas, and observe the luminosity of the flame. What commercial use has ethylene [R 395]? Hold a cold, dry beaker over the flame (?). What are the products of complete combustion of all hydrocarbons?

c Detach the nozzle, reattach the delivery tube to the exit tube, and lower the other tube of the washing-bottle once more. Place 1 c c of bromine [CAUTION!] in a test-tube, cover it with 5 c c of water, put the test-tube into a beaker filled with cold water, and allow the gas to bubble into the bromine. When the color of the bromine has disappeared, examine the contents of the test-tube (?). Is the product colored? Is it soluble in water? What do you infer as to its specific gravity? Detach the dropping-funnel, wash it out, and place in it the contents of the test-tube. Draw off the lower, oily layer into a dry test-tube and note its odor (?). Try its solubility in alcohol (?).

d Why is the accepted formula for ethylene preferred to the

simplest? What volume of oxygen would be required to burn one volume of the gas completely? What would be the relative volumes of the products at  $0^{\circ}$  and  $100^{\circ}$ , respectively? What volumes of bromine vapor and ethylene would be required for complete combination, and what would be the relative volume of the product (in the state of vapor)?

### 127 Acetylene

*a* Fill a test-tube with water and invert it in water in an evaporating-dish. Introduce a small piece of calcium carbide under the mouth of the tube (?). Test the water with litmus (?). Bring a light to the mouth of the tube (?). Note the luminosity of the flame, and compare with flames of methane and ethylene (?).

*b* Can you state a general method for making hydrides of non-metals (such as  $C_2H_2$ ,  $PH_3$ ,  $NH_3$ )? Can  $SH_2$  [R 526] and  $ClH$  [R 588] be formed similarly?

### 128 Flames

*a* Unscrew the tube of the Bunsen burner, turn on the gas, and light it (?). Turn off the gas and replace the tube. Make a drawing of the vertical section of the burner through the feed pipe (?).

Light the gas again and hold one side of the evaporating dish, first in the non-luminous flame and then in the luminous one (?). Which substance causes the light (?), and how? Why does this substance remain for a time suspended in the flame, instead of burning at once?

*b* Hold a splint across the luminous flame close to the bottom, and examine the wood (?). Inference (?). Repeat with the non-luminous flame (?). Why is the interior of the flame cold?

*c* Is any gas entering or escaping from the holes at the base? To answer this, light a splint, blow the flame out, and hold the smoking end close to the holes (?). Confirm by scattering a



very small amount of pulverized calcium carbonate on a piece of paper, and shaking it off so that it falls past one hole. Observe the flame (?)

Hold the burner up and blow a sudden puff of air towards one of the holes (?) What is the effect of increasing the supply of air?

*d* Light a taper and a splint. Blow out the flame of the taper and instantly apply the flame of the splint to the ascending "smoke" (?) Repeat, noting whether the taper can be relighted at a distance from the wick (?) Explain. Is the flame of a taper a gas flame or not?

*e* Pulverize a few particles of potassium sulphate. Take a small Bunsen flame and reduce the supply of air until a small luminous region appears. Heat the platinum wire, touch the salt with it, and hold the adhering powder steadily in the luminous part. After a minute or two, withdraw the bead, place it upon a clean silver coin and moisten with a drop of water (?) Explain the result. What are the reducing agents used here?

## CHAPTER XIX

### CARBOHYDRATES AND SUBSTANCES DERIVED FROM THEM.

#### 129 Starch and Glucose

*a* Shake about 0.5 c.c. of starch with 20 c.c. of water and then boil (?). Add a few drops of the liquid to 5 c.c. of Fehling's solution\* and warm the latter (?). Does starch change Fehling's solution?

Place three-fourths of the remaining starch suspension in a flask, set it on the wire gauze, add 5 or 6 drops of concentrated hydrochloric acid, and boil gently for ten minutes.

*b* While this is going on, cool the rest of the starch suspension in running water and pour it into a beaker full of cold water. Add one drop from 5 c.c. of a solution of potassium iodide in which a single crystal of iodine has been dissolved (?).

*c* Cool the contents of the flask (from *a*) and add sodium carbonate solution drop by drop, shaking between drops, and touching the edge of a piece of litmus paper with a glass rod dipped in the liquid, until the liquid gives a faint alkaline reaction.

Now add a few drops of this liquid to 5 c.c. (measured) of Fehling's solution and warm the latter [R 404, 507] (?). Add more of the liquid, boil again, and continue until the blue color is gone. It takes 0.005 g. of glucose to reduce and decolorize 1 c.c. of Fehling's solution. What amount of glucose was contained in the part of the liquid you added?

\* No. 1 69.3 g. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with water to make 1 liter. No. 2 350 g. Rochelle salt and 100 g. sodium hydroxide with water to make 1 liter. Mix equal volumes (measured) just before use.

**130 Sucrose**

*a* Dissolve about 0.5 g of sucrose (ordinary sugar) in 20 c c of water and repeat 129 *a* and *c* with this liquid. Does sucrose reduce Fehling's solution? Do acids hydrolyze it to give glucose?

*b* Dissolve about 0.5 c c of molasses in water and test for glucose as in 129 *a*, par 1 (?)

*c* Tabulate the physical and chemical properties of starch, glucose, and sucrose separately as follows: color (?), solubility (?), action on Fehling's solution (?), action of dilute acids (?)

**131 Ethyl Alcohol**

*a* Dissolve 20 g of glucose syrup in 150 c c of water. Break up a piece of yeast and add it to the syrup. Fill a flask (or bottle) to the base of the neck with the mixture, plug the mouth of the flask with cotton, and set the whole aside in a warm place for 3-4 days.

Fit to the flask a 1-hole stopper, L-tube, and rubber tube terminating in a straight glass tube. Take 15 c c of limewater in a test-tube, insert the glass tube to the bottom of this, and shake the fermented liquid in the flask (?). Note the gas evolved and its reaction with limewater (?). In what form of solution was the gas before the shaking [R 133]?

Filter the liquid and place it in a larger flask, fitted with a cork and L-tube, and connect (Fig 19, p 62) with a condenser [Storeroom]. Distil off about 50 c c. Place the distillate in a distilling-flask [Storeroom] fitted with a thermometer, connect with the condenser, boil with a small flame, and catch the part which passes over between 75° and 93°.

*b* Note the odor of the distillate (?). Test it with litmus papers (?). Saturate a tuft of asbestos wool with the liquid, set the tuft on the base of the stand, and apply a light (?). Hold a cold, w-m bottle over the flame, to recognize one product (?). Close the bottle and test the gas in the bottle by shaking with limewater (?). Make the equation for the com-

bustion (?) If you burned alcohol vapor and pure oxygen, what relative volumes should you use, and what relative volumes of the products (measured as gases) would be formed?

c To a few drops of the alcohol add 1 c c of sodium hydroxide solution. Pulverize one or two (not more) crystals of iodine, add a part of the powder to the mixture, shake vigorously, and warm (?). The amount added must not be sufficient to give a permanent brown tint to the liquid. The precipitate is iodoform  $\text{CHI}_3$  (related to chloroform  $\text{CHCl}_3$ ).

d Summarize the observed physical and chemical properties of alcohol (?).

### 132 Acetic Acid

a To 1 g of sodium acetate add some dilute sulphuric acid, and warm. Note the odor (?). How could you use this action to make acetic acid? How is it manufactured [R 407]?

b Take 5 c c of acetic acid. Test with litmus paper (?). Recall its interaction with zinc or iron (16 e) (?). To the acid add 3–4 g of litharge and boil gently for a few minutes (?). Filter, if necessary, while hot, and set the clear solution aside to crystallize (?). What is the common name of the product [R]?

c If, in 129 a, acetic acid had been used instead of hydrochloric acid, what modification in the directions would have been necessary?



Fig 29

### 133 Distillation of Wood

a Take three-fourths of a hard glass test-tube full of sawdust and wood chips. Arrange the apparatus as in Fig 29. The test-tube is inclined slightly downwards towards the mouth. The wide test-tube, in which the distillate is to be caught, is surrounded by cold water, and a nozzle is inserted in one of the holes in the stopper. Heat the contents of the test-tube, at first gently, and later strongly, until no more vapors are evolved.

During the heating, set fire to the issuing gas (?) Is the flame luminous, or not? Compounds of what element must be present?

Examine the condensed liquid. What liquid or liquids are seen? • Test the liquid with litmus papers (?) What dissolved substance causes this reaction [R. Wood, 408. Coal, 410-411]?

Examine, describe, and name the residue in the hard glass test-tube (?) Name five observed products from distilling wood (?)

• *b* Place a small piece of charcoal in a test-tube half full of water (?) Now hold it under the water with the reverse end of the file, and boil the water for several minutes (?) When the whole has cooled, test once more the tendency of the charcoal to float (?) Explain.

*c* Boil dilute solutions of litmus and indigo, separately, with pulverized animal charcoal, and filter each liquid (?) The activity of the charcoal is much increased by previous heating in a covered crucible.

#### 134 Coal

*a* Repeat 133 *a*, using bituminous coal. Test for hydrogen sulphide in the coal gas by holding a piece of filter paper, moistened with lead acetate solution, in the unlighted gas (?)

Name six observed products from distilling coal (?)

*b* *Coal Analysis* [Quant.] Weigh a dry porcelain crucible and lid or cover (?) Place in it 1 g. of coal and weigh again (?) Set the crucible, uncovered, in the air-bath at 105° for exactly one hour. Cover the crucible and, when cold, weigh it again (?) The loss in weight is the "moisture" [R. 409]. Calculate the per cent of moisture (?)

Now place the crucible, covered, on the clay triangle, about four inches above the mouth of a Bunsen burner. Heat it for eight minutes, in such a way that the flame heats the sides as well as the bottom of the crucible. Allow the crucible to cool (while covered), and weigh again (?) The loss in weight is

"volatile matter" Calculate the percentage of this in the original coal (?)

Finally, replace the crucible, without cover, in a slanting position on the clay triangle, and heat once more. Heat carefully, at first, to avoid loss by decapitation and ejection of particles. The complete burning of the "fixed carbon" may take several hours. When only a light-colored ash remains, cover the crucible, allow it to cool, and weigh again (?). Calculate the percentage of fixed carbon (?) and of ash (?)

Calculate the calorific power in B T U \* as follows

$$\text{B T U} = (\% \text{ fixed carbon} \times 14,670 + AV)/100,$$

where  $V$  is the per cent of volatile matter and  $A$  varies with  $V$  as follows

$$\begin{array}{ll} V = 2-15 \% & A = 23,400 \\ V = 15-30 \% & A = 18,000 \end{array} \quad \begin{array}{ll} V = 30-35 \% & A = 17,100 \\ V = 35-40 \% & A = 16,200 \end{array}$$

\* The calorific power is reckoned by engineers in British Thermal Units, 1 B T U being the heat required to raise one pound of water  $1^{\circ}\text{F}$ . Dividing the number of B T U by 1.8 gives the number of calories per 1 g.

## CHAPTER XX

### ORGANIC ESTERS AND SALTS COLLOIDS SOAP FOODS

#### 135 Formation and Hydrolysis of an Ester

*a* To 2 g of sodium acetate in a test-tube add 2 c c of ethyl alcohol and 1 c c of concentrated sulphuric acid. Agitate for a minute or two, warm very slightly (do not boil!), and note the odor [R 413] (?). This is a test for acetic acid or an acetate.

*b* Repeat, using amyl alcohol instead of ethyl alcohol (?).

*c* Place 10 c c of water in one test-tube and 0.5 c c of methyl acetate  $\text{CH}_3(\text{CO}_2\text{CH}_3)$ , an ester, in another. Test each with blue litmus paper (?), then mix and test again [R 414] (?). If the result is not definite, wait a few minutes and test the mixture once more (?).

#### 136 Soap and its Properties

*a* Mix in a test-tube 5 c c of cold, saturated sodium hydroxide solution and 5 c c of alcohol, shake, and allow to settle (?). Pour off the upper, alcoholic layer into another test-tube, add to it an equal volume of fat or cotton seed oil, and shake (?). Put the liquid into an evaporating dish on the wire gauze and set fire to the contents. Warm the dish with a very small flame to assist in driving off the alcohol. Stir until the flame goes out, and then stop heating. The pasty mass is soap, mainly sodium stearate and sodium palmitate [R 412], mixed with glycerine. Write an equation (?). Rub a little with water on the hands (?).

The alcohol is used simply as a common solvent for the fat and the alkali and is employed in the laboratory experiment to save time. •

*b* Dissolve the soap from *a* in a little warm distilled water and cool. To one-fourth of the solution in a test-tube add hydrochloric acid and shake vigorously [R 415] (?)

To show that the precipitate is an acid, withdraw it by means of a glass rod, suspend it in 10 c c of water in another test-tube, add a few drops of sodium hydroxide solution and heat until solution takes place. Write the equation (?)

To what class of substances does *b* show soap to belong?

*c* To another quarter of the soap solution add calcium chloride solution (?) Explain the action of hard water [R 415] on soap solution

*d* To the remainder of the cold soap solution, add sodium chloride solution (?) This is called "salting out" [R 415], and is a case of coagulating a colloid [R 417]. To what class of solutions does this show soap solution to belong?

### 137 Colloidal Suspensions

*a* Shake some arsenic trioxide with 25 c c of cold water vigorously for several minutes, filter, and to the filtrate add an equal volume of hydrogen sulphide solution. Arsenious sulphide  $As_2S_3$  is formed, but remains in colloidal suspension.

*b* Pour the suspension from *a* into a square bottle, and examine it in sunlight, or, better still, by holding it close to an incandescent bulb. Look first through it towards the light (?) Does it appear to be transparent and clear, or no? Now look at it from a position at right angles to the direction of the light, and answer the same question (?) With a microscope, the particles in such solutions can be perceived, individually [R 416].

*c* Divide the suspension from *a* between 5 clean test-tubes. Keep one, coiled, for reference. To one add sodium chloride solution (?), to another dilute hydrochloric acid (?), to the third calcium chloride solution (?), dissolve a little sugar in the fourth (?), and observe them from time to time. Note which coagulates last (?)

The positive ion is here the coagulating agent. How does



valence affect coagulating power? Do non-ionized, non-colloidal substances like sugar produce coagulation?

After a day or two, does the arsenious sulphide in the reference test-tube coagulate or settle of its own accord?

*d* Dissolve a single particle of iodon in 1 c c of alcohol. Add the solution to a test-tube full of water (?) Examine in the light as in *b* (?) Cork and keep, to see whether settling takes place (?)

*e* Summarize the special properties of colloidal suspensions (?)

*f* Boil 300 c c of distilled (or soft) water in a large beaker, and add to it, a few drops at a time, 3 c c of ferric chloride solution. The salt is thus somewhat hydrolyzed and contains suspended ferric hydroxide  $\text{Fe}(\text{OH})_3$ . Color?

Examine this suspension in the light as in *b* (?)

Take 5 test-tubes full of the dialyzed liquid, keep one for reference, and add to each of the others a very dilute solution (0.1 *N*) of one of the following coagulants: sodium chloride, sodium sulphate, sodium carbonate, calcium chloride. This colloid is coagulated by the negative ion. Note the amount and time required in each case (?) What is the effect of valence?

### 138 How Soap Cleanses

*a* Place 1 c c of kerosene in one test-tube and 1 c c of cotton seed oil in another. Add about 10 c c of water to each, shake vigorously, and place in the rack (?) Is a permanent emulsion formed?

Now add to each 2 c c of soap solution (ivory soap Aq 10), shake again, and observe as before (?)

*b* Boil 200 c c of water in a flask. Saturate the test-tube brush with ferric oxide (pulverized) suspended in cotton seed oil (6 g 100 c c) [Instructor] and push it into a test-tube. Add about 15 c c of the hot water, and work the brush in the tube (?) Does hot water alone remove the ferric oxide and oil?

Remove the brush, pour out the water, place 15 c c of hot

soap solution in the test-tube, and work the brush in the tube as before (?). Remove the brush, pour the contents of the test-tube into a 100 c c beaker, and rinse first the brush and then the test-tube with hot water, catching the rinsing-water in the beaker. Have the oil and rust been removed from the brush?

After a short time, examine the contents of the beaker (?). Where is the oil (?) and in what condition? Where is the rust (?) and is it free from oil?

Explain how soap solution removes grease or oil from a large object or a powder (?).

### 139 Tests for Food Components

*a Starch* Place water in a test-tube, add a pinch of starch, shake, and boil (?). How does the starch change? Cool the suspension in running water, and when it is cold (not before), divide it into two parts and to one add a drop of the solution of iodine in potassium iodide (?). Keep the other half for use in *c*.

*b* Take another pinch of dry starch, and add to it a few drops of the iodine solution (?). Tabulate the results of *a* and *b*, as well as those of *c*, *d*, *e*, *f*, and *g*, as follows

FOOD COMPONENT	REAGENT OR TREATMENT	RESULT
Starch (suspension)	Iodine sol	?
Starch (grains)	Iodine sol	?

*c Glucose* Shake about 0.5 c c of glucose in 5 c c of water. Add 5 c c of Fehling's solution (p 132, footnote) and boil (?).

*d Lactose (milk-sugar)* Repeat *c* with about 0.5 c c of milk-sugar (?).

*e Maltose from Starch* To 5 c c of the starch suspension prepared in *a* (which itself gives no reaction with Fehling's solution, 129 *a*), add about 1 c c of saliva, mix, and set aside for fifteen minutes. Then add 5 c c of Fehling's solution and boil (?). How was the maltose produced [423]?

*f Protein* To a few particles of egg albumin, add a few drops of concentrated nitric acid (?). Add some water to wash

off the acid, and pour away the liquid, leaving the solid residue. To the latter add a few drops of ammonium hydroxide (?). Repeat with a scrap of woolen yarn (?). Account for the effect of nitric acid on the skin and nails (?).

*g Fat* Place on small pieces of unglazed paper (1) a particle of fat, (2) a drop of cotton seed oil, and (3) part of a crushed almond, put them in the evaporating dish, and warm gently until the fat melts. Examine the papers (?).

*h Examination of a Food* Rub a small piece of raw meat in the mortar with a little water until the color is removed. Then apply to portions of the meat the tests in *a* for starch (?), in *f* for protein (?), and in *g* for fat (?).

*j* Take a small piece of sausage and apply to portions of it the tests in *a*, *f*, and *g*. If the results of *a* and *f* are not definite, dissolve away the fat by shaking the fragments of sausage with carbon tetrachloride, and try *a* and *f* again with the residue (?).

#### 140 Food Components of Milk

*a* Heat 50 c c of milk to boiling in the evaporating dish. With a glass rod, fish out the skin which forms on the surface and transfer it to a test-tube. Apply to it the test in 139 *f* for protein (?). Name the substance [R 422]?

To the milk add three or four drops of acetic acid and stir (?). How is this result to be classified? What sort of substances cause milk to curdle? What is the connection with "sour milk"? Filter the acidified milk and test the residue on the filter for protein (?).

*b* To 5 c c of the filtrate add 5 c c of Fehling's solution, and boil (?). What is shown to be present (139 *d*)?

*c* To 5 c c of the filtrate from *a* add iodine solution (?). For what food component is this a test? Is it present?

*d* Put a few drops of unboiled milk on a piece of unglazed paper and heat as in 139 *g* (?). Result?

*e*. Which food components have you found in milk?

*f Preservative — Formaldehyde* To 5 c c of milk in a test-tube add an equal volume of water and, by means of a glass rod, one drop (not more) of formaldehyde solution (1 %) and shake. Take 5 c c of concentrated sulphuric acid and add to it by a glass rod one drop of ferric chloride solution. Now hold the test-tube of milk almost, but not quite vertical, and pour the sulphuric acid in a continuous stream down the side of the tube so that it may go to the bottom and form a layer under the milk. What color appears where the liquids meet (?) Repeat with diluted milk free from formaldehyde (?)

#### 141 Food Components of Flour

*a* Take about 10 c c of flour, make it into a dough with water, and then place it in a small piece of cheese cloth. Bring the corners together and with a thread tie the cloth so as to enclose the dough in a bag.

Knead the bag in water in the evaporating dish so long as the liquid squeezed out appears to be more milky than that in the dish. Then pour the milky liquid into a beaker to settle. Take fresh water, and continue the kneading, until the milkiness almost ceases.

Open out the cloth and wash the contents in running water until the wash-water is no longer milky.

*b* Test portions of the residue in the cloth for starch (?), glucose (?), and protein (?), and record the results (?)

*c* Test a pinch of the dry flour for fat (?)

*d* Pour the water away from the sediment in the beaker from *a* and test portions of the solid for starch (?), glucose (?), and protein (?), and record the results (?)

*e*. Summarize the food components found in flour (?)

## CHAPTER XXI.

### SILICON AND BORON

**142 Silica** Mix 1 g of finely powdered silica with 4-5 g of anhydrous sodium carbonate. Coil the platinum wire to watch-spring form and, by alternately heating in the Bunsen flame or blast-lamp, and dipping in the mixture, obtain a large bead and heat it strongly till all action (?) seems to have ceased. Place the bead in a test-tube and make others by the same process. Dissolve the beads in a small amount of water. Add hydrochloric acid a drop at a time until the solution is strongly acid (?). Evaporate the solution to dryness on the sand bath (?). Treat the residue with warm water, wash the whole contents of the dish into a test-tube, and examine (?).

**143 Analysis of a Silicate** Mix dry potassium carbonate with anhydrous sodium carbonate in equal proportions in a mortar. Coil the platinum wire to watch-spring form. Mix a little powdered talc (is this soluble in water? What is its common name?) with 6-7 times as much of the "fusion mixture," and hold some of the result on the platinum wire in the flame of the blast-lamp till it is completely melted and all action (?) has ceased. Repeat till several beads are obtained. Treat the beads with boiling water in a test-tube until they are completely disintegrated. Filter through a small filter paper and wash the precipitate with water. Preserve this filter paper and precipitate for use later. Acidify the filtrate with concentrated hydrochloric acid and proceed as in 142, last two sentences (?).

Make a hole in the paper and wash the precipitate obtained

above into a test-tube. Add dilute hydrochloric acid, and warm (?). Filter, if necessary, and add ammonium hydroxide to alkaline reaction (?). The precipitate is aluminium hydroxide. Boil and filter. To the filtrate add a few drops of ammonium hydroxide, some ammonium chloride solution, and some sodium phosphate solution, and stir with a glass rod (?). Compare 117 c.

**144 Silicon Tetrafluoride** Mix intimately 1 g. of pulverized calcium fluoride with an equal weight of sand, place in a test-tube, and moisten the mixture with concentrated sulphuric acid. Apply a gentle heat (?). Hold a glass rod, with a drop of water at its lower end, in the gas and examine the rod (?).

#### 145 Boric Acid

*a* Pulverize some borax and make a strong solution in boiling water. Add concentrated hydrochloric acid until the solution is strongly acid, and set aside to cool (?). Filter off the crystals, wash with a few drops of cold water [Note 39, p. 116], and dry. Dissolve the crystals in the smallest possible amount of boiling water, and set the solution aside (?). Filter, and wash the crystals as before.

*b* Dissolve a part of the crystals in hot distilled water. Test this solution, and a sample of the distilled water, simultaneously with litmus paper (?). Dip a strip of turmeric paper in the same solution, wrap it round the upper part of the test-tube, and boil the solution until the paper is dry (?). Touch the paper with a glass rod dipped in sodium hydroxide solution (?). This is a test for boric acid.

Treat the rest of the crystals with cold sodium hydroxide solution (?).

*c* Place on separate parts of a watch-glass a drop of concentrated sulphuric acid, a drop of glycerine, and a very little pulverized borax. Rub the end of a platinum wire in each of these. Bring the end of the wire slowly up to the outer edge

near the bottom of a small Bunsen flame. How is the flame colored? This is a test for a borate.

An alternative method. Dissolve a small crystal of borax in 1-2 c.c. of water in a test-tube. Add a drop or two of concentrated sulphuric acid and then 2-3 c.c. of alcohol. Heat the mixture and set fire to the vapor of the alcohol (?).

#### 146 Borates

a Dissolve 1 g. of borax in distilled water. Test both this solution, and the distilled water, with litmus paper (?).

Put two drops of the solution into a test-tube and dilute with water till the tube is two-thirds full. To the remainder add silver nitrate solution (?). Add silver nitrate solution to the very dilute solution also (?). The difference is more marked if the dilute solution is first warmed. For comparison, add silver nitrate solution to an exactly equally diluted sodium hydroxide solution (?). What conclusion do you draw in regard to the action of water on borax? Write the equation, and explain.

b Heat a straight platinum wire in the Bunsen flame, and, while yet glowing, dip it into a small quantity of borax. Return the wire to the flame and observe the changes in the substance (?) until it forms a bead. Try borax beads, as directed in 2 d, e, and f, with cupric oxide (?), manganese dioxide (?), and ferric oxide (?), separately.

147 Identifying an Unknown Substance II Obtain [Instructor] a single unknown solid substance. It will either contain one of the following radicals, or be one of the substances mentioned.

orthophosphate	✓ acetate	glucose
metaphosphate	borate	ethyl alcohol
pyrophosphate		sulphur
carbonate	starch	a food
bicarbonate	sucrose	

The positive radicals will be limited to  $\text{NH}_4$ , Na, K, and Ca, of which only the first is to be identified. For foods, use methods

in 139 Record at the time the result of each observation  
Record negative results also

*a External Examination* Record the state (?), crystalline form (?), color (?), and odor (?)

*b Solubility and Reaction of Solution* Try the solubility of a few particles in water (?) and test the solution with litmus papers (?)

*c Effect of Heating* Heat 0.5 g in a dry test-tube Does it melt (?), char (?), or otherwise change (?), and does it give off gas or vapor? Odor?

If WATER VAPOR is given off (?), the substance may be a hydrate, acid salt, carbohydrate, or calcium hydroxide Incline the mouth of the tube downwards, drive all the water off, dry out the tube with filter-paper, and continue heating Does it now char (?), change (?), or give off gas or vapor?

A SUBLIMATE indicates a salt of  $\text{NH}_4$  Test 103 *d*

A COLORLESS GAS with NO ODOR may be carbon dioxide (test?)

A COLORLESS GAS with AN ODOR may be ammonia, sulphur dioxide, or gases from the charring of carbohydrates (?)

*d Action of Concentrated Sulphuric Acid* To 0.5 g add 2-3 drops (not more) of concentrated sulphuric acid (?) If necessary, warm gently (?)

If the substance turns black, it is a carbohydrate (?) Ascertain which one by the proper test (129, 130)

A COLORLESS, ODORLESS GAS may be carbon dioxide (test?).

A GAS with an ODOR may be acetic acid (test?)

If there is NO GAS (no bubbling), the substance may be a phosphate or a borate (test?)

*e Report* State your conclusion, with the reasons therefor (?)

*f* Obtain a second unknown and proceed as before (?)

*g* Obtain a third unknown, involving exercise 113 as well as 147 (?)



## CHAPTER XXII

### METALLIC ELEMENTS OF THE ALKALIES

#### 148 Potassium Hydroxide.

- \* a Dissolve about 30 g of potassium carbonate [Notes 10, 11, 12, p 2] in 200-300 cc of water in a large beaker, and heat on a wire gauze to boiling. Slake 15-20 g of quicklime in a beaker (?), using heat if necessary to start the action, and make the product into a very thin paste with water. Add this gradually, and with constant stirring, to the boiling solution (?). Continue boiling for a few minutes (why?). Let the mixture settle, and, when it is cold, decant the clear liquid (or filter rapidly). Use the solution in b, c, and d.

Is calcium hydroxide appreciably soluble (Appendix IV)? Is calcium carbonate more or less soluble than is the hydroxide? Formulate the action and explain why it went to completion. What kind of hydroxides alone can be made by this method? Which hydroxides are of this kind (Appendix IV)?

- b Find the strength of the solution made in a by titration (alkalimetry). To do this, place a carefully measured volume (about 10 cc) of the clear solution in a small flask. Dilute with about four times its volume of water, as the concentrated solution is apt to decompose the indicator. Fill a burette to the very top of the nozzle with "normal" [R 124] hydrochloric acid. \* Add some phenolphthalein solution to the alkali and run in the

\* Or normal oxalic acid may be prepared (two students working together), and used here. Calculate the weight of pure [Instructor], crystalline oxalic acid [R 413] required to make 500 cc of normal oxalic acid solution [R 124]. Weigh out [quant] this amount on glazed paper and transfer it to a 500 cc graduated flask [Store room]. Dissolve the acid in distilled water and then fill up the flask to the mark.

acid cautiously until the red color just disappears. Note the volume of acid used (?). Calculate the concentration of potassium hydroxide in terms of a normal solution as unity (?).

c (Two students working together.) If the alkaline solution is above normal, calculate the volume of the solution required to make 100 c.c. of normal alkali. Place the necessary amount of the solution in a 100 c.c. graduated flask [Storeroom] and fill to the mark with water. (If the solution is less than normal, calculate and use the amount required for 200 c.c. of semi-normal alkali.)

Measure (burette) 5 c.c. of acetic acid into a flask and dilute with about 20 c.c. of water (or take 25 c.c. of commercial vinegar), add phenolphthalein, titrate with the normal (or semi-normal) alkali, and calculate the normality of the acetic acid (or vinegar) used (?). Calculate also the percentage of acetic acid present (?).

d Place very small quantities of the following solutions in separate test-tubes, dilute with water, and add excess of the solution of potassium hydroxide from *a* to each, ferric chloride (?), cupric sulphate (?), mercuric chloride (?). Describe the color and structure of the precipitates [Note 40, below]. Boil the contents of each test-tube (?). Do the precipitates dissolve or change in any way?

What kind of hydroxides can be made by this method? Do any metals fail entirely to form hydroxides [R 440]?

e Pulverize a small piece of potassium hydroxide and leave it exposed to the air on a watch-glass for 24 hours, or more (?). To a part of the product add dilute hydrochloric acid (?). Simultaneously, expose a small piece of sodium hydroxide and treat it in exactly the same way (?). Compare the results and explain.

*Note 40* — The **structure of a precipitate** may be described as gelatinous, flocculent, curdy, pulverulent, granular, or crystalline. What circumstances will determine the structure of a precipitate? Hereafter, describe every precipitate by terms like these.

## 149 Potassium Nitrate

a Dissolve 25 g of sodium nitrate and 22 g of potassium chloride in 50 c.c. of water and evaporate to half the volume on the sand bath. Fit a filter paper into a small funnel [Note 24, p. 10]. As rapidly as possible decant the hot, clear liquid from the crystals and set it aside. Throw the crystals which appeared during boiling at once on to the filter, and rapidly press out the rest of the mother-liquor with a spatula. Examine the form of the crystals and ascertain what they are (?). (If they are too small, recrystallize a part slowly from water in a beaker in order to learn their form.) When the decanted liquid is cold, press the product on a filter likewise. Examine this set of crystals as before (?). Compare both with the original substances.

To understand the process, write in the blank places of the table (below) the solubilities (grams dissolved by 100 g. water) of the substances concerned (Appendix V)

	10°	100°		10°	100°
Potassium nitrate			246	Potassium chloride	
Sodium chloride				Sodium nitrate	

Which of these substances will first be deposited from the boiling liquid? Ascertain by calculation how much of it (roughly) will be deposited at 100°, how much more will come out when the liquid cools, and how much will remain in the mother-liquor. What other substance will be present in large quantity in the hot mother-liquor, and how much of it must there be? How much of this product will be deposited when the liquid cools, and how much will be lost by remaining dissolved? What per cent of the possible yield of potassium nitrate may we expect to get? Dry your product, weigh it, and calculate what per cent was secured.

Explain why purer potassium nitrate can be obtained by crystallizing the product once more from water.

b Mix intimately in the mortar 5 g of finely pulverized potassium nitrate with 2 g of charcoal, and drop the mixture in

small portions into a red-hot crucible (?) What gases are evolved? What is the residue (test with an acid)?

*c* Pulverize 5 g of potassium nitrate and mix on paper [CAUTION] intimately with 2 g of flowers of sulphur. Throw the mixture [HOOD] in small portions into a red-hot crucible (?) What gases are evolved? Dissolve the residue and add barium chloride solution (?) Explain the explosive power of gun-powder (?)

**150 Potassium Cyanide [Poison]** How is this salt made [R 451]? Place 1 c c of potassium cyanide solution in an evaporating-dish, heat it, and add yellow ammonium sulphide solution until the color (?) no longer disappears. Evaporate to complete dryness [HOOD]. Dissolve a part of the residue with water, and add ferric chloride solution (?) A black precipitate (?) indicates that the heating was not sufficient. If this appears, heat the residue once more and try the action of ferric chloride again. In the first part of this experiment, what property of the cyanides, and which kind of ionic chemical change, are illustrated? Is this change instantaneous, as is the union or disunion of ions?

#### 151 Reactions of Potassium Salts

*a* Heat a little solid potassium nitrate on a clean platinum wire. Notice the color of the flame and examine with the spectroscope. Make a diagram showing the position of the lines with reference to the D line (in the yellow), which, on account of the sodium present, is shown by all flames in the laboratory.

*b* Saturate 10 c c of warm water (40°) with potassium nitrate. Add this solution to an equal volume of tartaric acid solution in a beaker (?) Agitate and cool in a stream of water (?) Note, also, the effect of rubbing the inside of the vessel with a glass rod. Describe the product [Note 40, p 148]. Filter, and wash the precipitate with a little alcohol.

*c* Dissolve a few particles of the precipitate from *b* in a drop

or two of warm water and test with litmus (?) Remembering that tartaric acid  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  is a dibasic acid, what sort of salt must the product be?

To a few particles of the precipitate add dilute hydrochloric acid (?)

To a part of the precipitate add drop by drop potassium hydroxide solution (shake between drops), using as little of the base as possible (?) To the resulting solution add concentrated hydrochloric acid a drop at a time. No effect can be expected until after the mixture becomes acid (test?). Stir vigorously with a glass rod, and cool in running water between drops (?) Finally, try the effect of excess of the acid (?)

*d* Heat the rest of the precipitate strongly in an open porcelain crucible (?) Extract with hot water, filter, and add any acid to the filtrate (?) The ignition of all potassium or sodium salts of organic acids gives the same result.

*e* Take 2-3 c c potassium chloride solution and, in another test-tube, dilute a few drops of it with 10 c c of water. Then add some picric acid solution to each portion [Note 40, p. 148] (?) Explain the difference in behavior (?)

What substance is shown to be present in a solution when we get the tests in *b* and *e*?

#### 152 Ammonium Salts

*a* What is a common effect of heating ammonium salts (103 *f*)? Heat 1 g of ammonium phosphate in a hard glass test-tube (?) Dissolve the residue in water and test with litmus paper (?)

Do all salts of ammonium give ammonia when heated (101 *a*, 109 *a*)? Is simple heating a test for an ammonium salt? Observe the odors of all the salts of ammonium (solids and solutions) in your kit, or upon the side-shelf (?), and explain.

*b* Do ammonium salts impart color to the flame?

*c* Take a solution of any ammonium salt and divide it into three portions. To one add excess of tartaric acid solution, and

shake (?) To the second add picric acid solution (?) Compare these results with 151 *b* and *c*. To the third add sodium hydroxide solution and note the odor (?) How should you distinguish ammonium-ion from any other ionic substance? Why is heating the salt not a sufficient test (103 *c*)?

*d* Test ammonium chloride solution with litmus (?) Do you infer that ammonium hydroxide is a very inactive base [R 437]?

### 153 Sodium Carbonate by Solvay Process

*a* Take 75 c c of ammonium hydroxide, dilute with 25 c c of water, and dissolve in it 25 g of powdered ammonium carbonate by shaking (ammonium hydroxide solution is used instead of water in order to secure ultimately a higher concentration of ammonium-ion, and therefore of  $\text{HCO}_3^-$  ion, than could be obtained with the carbonate alone, the solubility of this salt being too small). Then saturate the solution completely with sodium chloride by prolonged agitation with finely powdered salt in a corked bottle. If crude salt is employed, it should be washed with water before use. Decant the clear liquid into another bottle, fitted with cork and two tubes, one of which reaches to the bottom. If, because of delay, a dense precipitate has appeared, proceed without decanting. Through the latter (long) tube, pass in carbon dioxide from the laboratory supply, or from a Kipp's apparatus or generator, until the solution is saturated. This operation may occupy an hour or more. During the absorption of the carbon dioxide, the exit tube should be closed to prevent waste of the gas. Finally, close the tubes with caps of rubber tubing plugged with glass rods and set aside over night (?) Filter off the deposit, and dry by pressing between filter papers.

*b* Dissolve in water a little of the solid from *a*, which must have ceased to smell of ammonia (why?), and test the reaction of the solution with litmus (?) If the solution is not acid, explain why it is not so.

To part of the solid add any dilute mineral acid (?)

c Heat the rest of the solid in a test-tube clamped so that the mouth is inclined slightly downward, and ascertain what gases and vapors are evolved (?) When gas ceases to be given off, dissolve the cold residue in a very little water, test the reaction of the solution with litmus paper (?), and set it aside to crystallize in an open dish (?) Explain the reaction with litmus (?) Dry the crystals, and ascertain the effects upon them of (a) addition of an acid (?), and (b) of exposure on a watch-glass (?)

Compare the solubilities of the carbonate (Appendix IV) and bicarbonate of sodium [R 461], and explain why the bicarbonate is made first and then the carbonate from it

**154 Reactions of Sodium Salts** Take some salt of sodium and try the flame test, and examine the flame with the spectroscope as in 151 a Take a solution of some salt of sodium, and add to one portion picric acid solution (?), and to the other tartaric acid solution (?) Compare all the results with those obtained in 151 and 152 b and c

How could you distinguish sodium, potassium, and ammonium salts from one another? How could you demonstrate positively the presence both of a potassium and of an ammonium salt in a mixture of the two without the aid of the flame test or spectroscope?

Which salts of potassium, ammonium, and sodium are least soluble?

**155 Baking Powder** Weigh out 2 g of potassium bitartrate (cream of tartar) Write the equation for its interaction with sodium bicarbonate (?) Calculate how much of the latter salt will be required (?) Weigh out this amount, and mix the two salts on paper In practice, corn starch is also added (Why?), but is not here required

Put half the mixture in cold water in a beaker (?) Put the other half in water previously heated (?) Why do soda biscuits rise so rapidly when placed in the oven?

**156 Qualitative Analysis of Baking Powder**

*a Preparatory* Place about 4 c c of the baking powder into a large test-tube, add 20 c c of water, and shake vigorously for several minutes. Filter the liquid and test the clear filtrate as in *c*, *d*, *e*, and *f*.

*b Starch* (see 129 *b*) Perforate the filter paper and with water wash some of the residue into a test-tube. Boil this suspension, and then cool it and fill the test-tube up with water. With a glass rod, add to the suspension one drop of a solution of iodine in potassium iodide (?). A blue color indicates starch.

*c Tartrate Radical* Place 4 c c of the filtrate from *a* in an evaporating dish with 5 drops of concentrated sulphuric acid and evaporate to dryness over a small flame. Charring and an odor of burnt sugar indicate a tartrate.

*d Phosphate Radical* (see 116 *c*) Take 1 c c of the filtrate from *c* and acidify with 1 c c of dilute nitric acid. To 5 c c of ammonium molybdate solution add 3 drops of this mixture, warm, and set in the rack (?). Phosphates give a yellow precipitate.

*e Sulphate Radical* (see 86 *b*) Acidify about 5 c c of the filtrate from *a* with 5 c c of dilute hydrochloric acid and add barium chloride solution (?). What is the precipitate (if any)?

*f Ammonium Radical* (see 103 *d*) To 5 c c of the filtrate from *a* add 5 c c of sodium hydroxide solution. Heat to boiling and note the odor (?) and reaction of the vapor (not the liquid) towards moist red litmus paper (?). What is the gas (if any)?

*g Calcium Radical* Shake about 0.5 c c of the baking powder with 5 c c of dilute hydrochloric acid. Filter and to the filtrate add ammonium hydroxide until the liquid is alkaline to litmus. Now add acetic acid until the solution is acid to litmus, boil, and filter if the liquid is not clear. Add am-



monium oxalate solution (Sec 51 a) The precipitate, if any, is calcium oxalate

*h Aluminum Radical* For test, see 189 *f* A blue color indicates aluminum

*j Report* Summarize, stating which radicals were present and which absent (?)

#### 157 Ionic Equilibrium and the Ion-Product Constant

*a* Dilute a few drops of methyl orange solution [R 258] with much distilled water Add a few drops of an acid (?) and then excess of a base (?) What colors does this indicator show in neutral, acid, and alkaline solution, respectively? What ionic substance is present in the acid, and absent from the other solutions?

Take some distilled water in a beaker and add to it 2-3 drops of methyl orange solution, and divide the liquid between three test-tubes To the first two add a little acetic acid (?), to the third a drop of hydrochloric acid (?) To the first add now some solid sodium chloride, and shake (?) To the second add some solid sodium acetate, and shake (?) What ionic substance has disappeared? Explain the difference in behavior [R 468] To the third add solid sodium chloride, and shake (?) Explain the absence of effect

In what way did 68 *b* illustrate the same principle?

*b* Take three portions of a saturated solution of potassium chlorate in as many test-tubes (If there is any deposit in the bottles, this and the following solutions must be shaken before use to insure saturation) To the first add saturated sodium chloride solution (?), to the second saturated potassium chloride solution (?), to the third saturated sodium chlorate solution (?) Allow them to stand for a minute or two before drawing any conclusion Explain [R 470-471] The experiments will fail if all the solutions are not saturated

*c* To 1-2 c.c. of concentrated hydrochloric acid add concentrated sulphuric acid drop by drop (?) Explain

**158 Purification of Sodium Chloride**

*a* Prepare about 150 c c of a cold saturated solution of common salt by grinding the salt for some time in a mortar with the water. If crude salt is used, it must first be washed with water. Place the solution in a beaker, and pass hydrogen chloride into the solution. Prepare this gas by placing a handful of common salt in a generating-flask (Fig 17, p 51), covering it with concentrated hydrochloric acid, and allowing concentrated sulphuric acid to fall into it from a dropping-funnel. The hydrochloric acid prevents frothing and steadies the stream of gas (why?) Deliver the gas into the solution through a thistle-tube with the mouth downward (?). When considerable precipitation has occurred, filter by putting a clean silver coin with milled edges in a funnel, pouring the liquid and crystals upon it, and pressing with a spatula.

Why is the thistle-tube preferable to ordinary tubing?

*b* Explain why, in *a* the salt is precipitated. If the crude salt had contained other salts, which of them would have been affected by the introduction of hydrogen chloride, and which not? Specifically, would sodium sulphate or magnesium chloride have been affected, and how? If either of these would be affected and had been present, under what circumstances might it have entered into the precipitate (Appendix IV)? Within what limits, then, does the process give a means of purification?

## CHAPTER XXIII

### METALLIC ELEMENTS OF THE ALKALINE EARTHS

#### 159 Marble and Quicklime

*a* Select two small granules of marble. Place one on the wire gauze and heat with the full flame for 10 minutes (meanwhile proceed with *c* and *d*). Examine it and compare its appearance with that of the unheated fragment (?). Write the equation for the change (?).

*b* Place two strips of red litmus paper in two watch-glasses. Lay one of the fragments from *a* on each, and moisten with water carried on a glass rod (?). What sort of oxide is calcium oxide?

How may the decomposition of the marble be arrested (?) and reversed (?) without altering the temperature? What conditions permitted complete decomposition to take place here?

*c* Place about 1 g. of powdered fresh quicklime in a test-tube, add dilute hydrochloric acid, shake, and warm if necessary (?). What sort of oxide is quicklime?

For comparison, take a chip of marble and cover it with dilute hydrochloric acid (?). What is the reason for the difference?

**160. Reactions of Calcium Salts.** Diluted calcium chloride solution [Note 41, below] may be used for *b*, *c*, *d*, and *e*.

*a* Try the flame test with a particle of solid calcium chloride and examine with the spectroscope (see that the platinum wire is clean. Note 42, below). Make a sketch of the spectrum showing the positions of the lines with reference to the sodium and potassium lines.

*b* To a part of the solution containing calcium-ion add

ammonium oxalate solution in excess (?) Filter off the precipitate and divide it into two parts Place each part in a test-tube, and treat one with dilute hydrochloric acid (?) and the other with diluted acetic acid (?) Explain this difference in behavior towards hydrogen-ion [R 481-483] Why was ammonium oxalate used in preference to oxalic acid?

What are the approximate numerical values of the ion-product constants of calcium oxalate, calcium carbonate, and calcium sulphate (Appendix IV)?

*c* To the second portion of the solution containing calcium-ion add some dilute hydrochloric acid, mix, and then add ammonium oxalate solution (?) Explain [R 482] If any precipitate appears, add more hydrochloric acid Now add a large amount of sodium acetate solution (?) What is the precipitate (calcium acetate is soluble), and why is it formed [R 484]?

*d* To the third portion of the solution containing calcium-ion add ammonium carbonate solution (?) Warm, if necessary Filter, divide the precipitate and treat parts of it with hydrochloric acid (?) and much diluted acetic acid (?), respectively Explain the result (?) Explain also the difference in behavior of the oxalate and the carbonate of calcium towards acetic acid, taking account both of the solubilities of these salts, and of the fundamental difference in behavior between oxalic and carbonic acids

*e* To the fourth portion of the solution add excess of dilute sulphuric acid (?) Filter Reserve the filtrate for *f*. Pierce the filter-paper and wash a small part of the precipitate into a test-tube Add some concentrated hydrochloric acid (?) Explain the change, if any occurs (?)

*f* Divide the clear (if not clear, filter again) filtrate from *e* into 3 parts To one small part add an equal volume of alcohol (formation of all precipitates, if long delayed, may be hastened by vigorous stirring) (?).

Neutralize (test?) the second portion with ammonium hydroxide (why?), add ammonium oxalate solution (?), and explain. Is the sulphate or the oxalate of calcium more soluble? Confirm your inference by giving the solubilities (Appendix IV).

To the third portion of the filtrate from *c* add a little sodium carbonate solution (?). Is the carbonate or the sulphate of calcium more soluble? What are then actual solubilities? How may permanent hardness be removed?

*Note 41* — In this and all following paragraphs headed "reactions" where "diluted" solutions are spoken of, the solutions must be diluted with 3-4 volumes of distilled water to secure good results.

*Note 42* — After use, the platinum wire must be cleaned. Form upon it a borax bead, and cause the molten bead to traverse the wire from end to end several times. Throw off the bead. Heat the wire persistently in the Bunsen flame, dipping it from time to time in hydrochloric acid (why?), until the wire no longer colors the flame. If much corroded, the wire may be boiled in nitric acid before being heated.

### 161 Hard Water

*a Soft water* To about 10 c c of distilled water add soap solution (12 g per 1 liter), drop by drop, shaking between drops. Count the number of drops required before a "permanent" lather or froth is obtained (?). A "permanent" froth is defined as one which persists for three minutes.

Give the name and formula of one typical component of soap?

*b Temporary hardness* Take 5 c c of freshly made, saturated lime-water (17 g  $\text{Ca(OH)}_2$  per liter) and add an equal volume of distilled water. Pass carbon dioxide through the half-saturated lime-water steadily until two changes (?) have occurred (meanwhile proceed with *c*). Write two equations, one for each change [R 384] (?). The clear product is water of temporary hardness. What substance is present?

*c Calculation of the degree of hardness* What weight (grams) per liter of calcium hydroxide was contained in the diluted lime-water? What weight (grams) per liter of  $\text{CaCO}_3$  would this

give in the final product (?) How many degrees of hardness is this in French units [R 489]? How many grains per U S gallon of 58,333 grains?

*d. Action of hardness on soap* To 2 c c (measured) of the product from *b* add soap solution (noting how much) and shake until a "permanent" lather is obtained (?) The precipitate is a calcium soap Write the formula of a typical component of this soap (?), and the equation for its formation (?)

*e Removing temporary hardness (softening)* To 2 c c (measured) of the product from *b*, add 1 c c (measured) of saturated lime water and shake (?) What is the precipitate [R 490-491]? Now add soap solution, noting how much is required to form a "permanent" lather (?) Was the amount required as great as in *d*, or was it nearer the amount used in *a*?

*f* Boil 2 c c (measured) of the product from *b* (?) What is the precipitate? When the liquid is cold, add soap solution as in *e*, to determine whether the hardness has changed (?)

*g Permanent hardness* Dissolve a crystal of magnesium chloride in 10 c c of water, add soap solution and shake (?) Write the equation (?) and name each substance (?)

*h* Test the city water with soap solution (?)

### 162 To Determine the Hardness of a Water, and the Weight of Soap Destroyed by Ten Gallons [Quant]

*a* Fill the burette with a solution containing 12 g of Castile soap per liter of 65 per cent alcohol \* In a 500 c c bottle, provided with a cork, place 100 c c of the hard water Run in the soap solution, 0.5 c c at a time, shaking vigorously after each addition until a "permanent" (161 *a*) lather is obtained If 12 c c (or less) of the soap solution is not sufficient, stop at that point, throw out the sample, take 50 c c of the hard water

\* This solution approximates closely to that used for determining hardness If accurately standardized, 1 c c of this solution, when added to 100 c c of a sample of water of 1° hardness (French, 1 part  $\text{CaCO}_3$  per 100,000) gives a permanent lather With 2° hardness, 2 c c are required per 100 c c of water, and so forth

diluted with 50 c c of distilled water, and start again. With very hard water it may be necessary to use as little as 5 c c diluted with 95 c c of distilled water. More than 12 c c of the alcoholic soap solution must not be used, because the alcohol then tends to prevent the formation of the lather and renders the results inaccurate. If only 5 c c (for example) of the water is used, then the amount of soap solution that would have been required for 100 c c is obtained by multiplying the volume of soap solution employed by 20. Record the results as follows

Vol of hard water used	c c
Vol of soap solution employed	c c
Vol of soap solution required for 100 c c of the water	$x$ c c

If the soap solution was standardized,  $x$  is also the degree of hardness in French units,  $2e$ , in parts per 100,000 (?). Convert this into U S or British units [R 489] (?)

b. Since 1000 g (1 liter) of the soap solution contained 12 g of soap, 1 c c contained 0.012 g of soap, and 100 c c of the hard water destroyed 0.012 g of soap (in 1 c c of the solution) for each degree of hardness

Hence 100 g of the hard water destroyed  $x \times 0.012$  g of soap. Hence 100 lbs of the hard water destroyed  $x \times 0.012$  lbs of soap. Or 1 lb of the hard water destroyed  $x \times 0.00012$  lbs of soap.

Now 10 gallons (U S) of water weigh 83.4 lbs. Hence 10 gal of the hard water destroyed  $83.4 \times x \times 0.00012$  lbs of soap. Weight (lbs) of soap destroyed by 10 gal (?)

Ten gallons (Brit) of water weigh 100 lbs. Weight (lbs) of soap destroyed by 10 gal (?)

**163 Reactions of Strontium Salts.** Use diluted [Note 41] strontium chloride solution for  $b$ ,  $c$ , and  $d$ .

$a$ . Same as 160  $a$ .

$b$ . Add ammonium carbonate solution and heat (?).

*c* Add dilute sulphuric acid (?)

*d* Add a clear solution of calcium sulphate (made by shaking a little of the pulverized salt with distilled water and filtering until clear) (?) The precipitate may come slowly Explain

**164 Reactions of Barium Salts** Use diluted [Note 41] barium chloride solution for *b*, *c*, and *d*

*a*, *b*, *c* Same as **163 a**, *b*, *c*

*d* Add a clear solution of strontium sulphate (made by shaking the salt with distilled water and filtering) (?) Explain. Now add concentrated hydrochloric acid (?) Why does the precipitate not behave like that in **160 c**?

Compare with **163 d**, and arrange the sulphates of these three metals in the order of solubility Give two methods of distinguishing the compounds of the elements in this family Examine the table of solubilities (Appendix IV) and suggest other ways of distinguishing calcium-ion and barium-ion, respectively, from the other two How could you tell a solution containing the ions of a member of this family from one containing those of the members of the previous family?

**165 Identification of Unknown Substances** Take three dry test-tubes, apply to the instructor for three "unknown" substances, and ascertain what each is Record negative as well as positive results (?)

*a* Study (1) Physical appearance (?)

(2) Odor (?)

(3) Solubility in distilled water and reaction of the solution toward litmus (?) After the final conclusion has been reached, reexamine the results recorded under (1), (2), and (3), and consider if the substance found has the properties there noted All results require checking in some such way

*b* (4) Identify first the negative radical, using the methods described in **113** and **147** (?)

Before beginning (4), make a list of all the negative radicals known to you, and place opposite to each the gases, if any,



which salts containing that radical, when heated, might be expected to give off. Consider also the means of recognizing these gases, if formed.

Before heating with a drop or two of concentrated sulphuric acid make a list of the reactions of sulphuric acid with salts containing each of the negative radicals. Consider also the means of recognizing such of the possible products as are volatile.

c (5) Dissolve the substance in distilled water (if insoluble, try dilute hydrochloric acid). Identify now the positive radical, using the reactions for the metallic ions just studied (?).

d (6) Write out the experiments and reasoning carefully in your note-book, and make sure that they prove the substance to be the one you finally decide that it is, and exclude the possibility of its being any other. See (3), above (?). Report the result to the instructor.

## CHAPTER XXIV

### COPPER AND SILVER

#### 166 Cuprous Chloride

*a* Dissolve about 2 g of cupric chloride in 15 c c of water in a small flask. Add 2-3 c c of pure, concentrated hydrochloric acid and about 5 g of metallic copper, and boil [Hoon] until the green tint is no longer perceptible in the dirty yellowish-brown color of the product. If a few drops added to a test-tube full of water, previously boiled to remove dissolved oxygen, confer a blue tinge upon the water, the action is still incomplete. What ion confers the blue tinge? What change do the cupric ions undergo? Is the change an oxidation or a reduction of cupric chloride?

*b* To a small part of the solution, when cold, add excess of sodium hydroxide solution (?). Why is so much of this required? Preserve the mixture in a corked test-tube for use in 168.

*c* Pour the rest of the solution from *a* into a large amount of water in a beaker (?). Expose some of the solid product, while covered with water, to the sunlight (?).

*d* To the rest of the solid product from *c* add concentrated hydrochloric acid, and shake (?). What is the complex negative ion here formed [R 504, 505-6]? Does it give a greater or a less concentration of cuprous-ion than does the insoluble cuprous chloride? Upon this basis explain the process of solution here observed. Pour a little of the solution into much water (?).

*e* To the rest of the solution made in *d* add a little chlorine-water (?). What ionic substance is shown by its color to be present? Pour this solution into much water (?) \*.

Define this form of oxidation, and the form of reduction in *a*, in terms of ions

**167 Cupric Hydroxide**

*a* To 1-2 c c of diluted cupric sulphate solution add excess of sodium hydroxide solution (?) Take one-third of this mixture and boil it (?)

*b* Boil 1 g of sugar dissolved in water (or use diluted glucose syrup) with a few drops of dilute sulphuric acid for several minutes (?) This gives glucose and fructose [R 405] Add this glucose solution to another portion of the mixture from *a*, warm gently (?), and note all changes Make no equation for the action of the glucose

*c* To the remainder of the mixture from *a* add ammonium hydroxide, and shake (?) What complex ion possesses this blue color [R 507]? Does this ion give a greater or a less concentration of cupric-ion than does the insoluble hydroxide? Upon this basis explain the process of solution here observed

**168 Cuprous Oxide** Divide the mixture from 166 *b*, containing a precipitate of hydrated cuprous oxide, into three parts

*a* Shake one persistently with air in a bottle, admitting fresh air from time to time (?)

*b* Boil the second portion (?)

*c* To the third portion add ammonium hydroxide (?) What is the color of the mixture? What complex ion is formed [R 507]? Why is cuprous oxide dissolved by ammonium hydroxide solution?

Shake this solution with air What ion is formed? Is the action more or less rapid than in *a*, and why?

**169 Cuprous Iodide** Dilute a few drops of cupric sulphate solution and add potassium iodide solution (?) Filter Wash the precipitate [Note 39, p 116] (?) What is the color (?) of the precipitate, and what is it? Add part of the filtrate to some starch emulsion (?) Shake the rest with some chloroform (?) Read the footnote on p 12

**170 Reactions of Cupric Salts** Use diluted cupric sulphate solution. What is the color of cupric sulphate itself? To what is the color of the solution due?

*a* Test the reaction of the solution with litmus paper (?) and explain [R 437]. Is copper an active metallic element?

*b* Lead hydrogen sulphide through another portion (?). Is this action reversible, theoretically? Add dilute sulphuric acid (?). Do dilute acids act upon any sulphides (80 g)? Why not upon this one [R 273]?

*c* To another portion add potassium ferrocyanide solution [R 510] (?)

*d* Note here the interaction (73 a) of zinc with cupric-ion (?)

*e* Make a borax bead and heat with it a minute particle of cupric oxide in the oxidizing (?) and in the reducing (?) flame, as in 2 e. The latter requires patience. If cupric sulphate had been used here, what reaction would have taken place [R 288]?

*f* Prepare a match (or splinter of wood) as in 92. Place on the end a moistened mixture of any copper salt with anhydrous sodium carbonate and heat in the reducing region of a small Bunsen flame. Break up the charred stick in water in a mortar, wash away the lighter particles, and rub the residue hard with the pestle (?)

**171 Ammonio-cupric Compounds** To a diluted solution of cupric sulphate add ammonium hydroxide (?), first a drop (?), then in excess (?). Of what ion does the copper now form a part? Do other compounds of copper yield the same ion (187 c)? Which action of all those in 170 and 171 should you hold to give the most delicate test for cupric-ion?

Try with the blue solution the tests in 170 *b*, *c*, and *d* (?). Are the concentrations of cupric-ion given by cupric sulphide (?), cupric ferrocyanide (?), cupric sulphate (?), and cupric hydroxide (?), larger or smaller than the concentration of free cupric-ion given by ammonio-cupric-ion? Which of these com-

pounds would be dissolved by ammonium hydroxide solution, and which not?

**172 Cuprocyanides** To 3 c c of a diluted solution of cupric sulphate add potassium cyanide solution [CARE! POISON], first a drop (?), then in excess (?) Does the solution show the color of cupric-ion? In what form of combination is the copper [R 508]?

Divide the solution into three parts and try the tests for cupric-ion given in 170 b and d, using in d a piece of granulated zinc (?) Would cuprous sulphide dissolve in potassium cyanide solution? Explain your answer Does cuprous sulphide (?) give larger or smaller concentrations of free copper ions than does the cuprocyanide? Would potassium cuprocyanide give the bead test (170 e) or the match test (170 f)?

**173 Double Salts (Potassium-Cupric Sulphate)**

a Saturate water at 70° with 5 g of finely powdered potassium sulphate (about 25 c c will be required) Calculate the weight of crystallized cupric sulphate which must be taken to get an equimolecular proportion, and dissolve it in its own weight of hot water Mix the two solutions, taking care not to allow any undissolved fragments of either salt to get into the mixture, and set the result aside to crystallize (?) Examine the form of the crystals and compare with those of blue vitriol (?) Dissolve a part of the crystals in water and use portions of the solution for b

b With the solution try tests in 170 b, c, and d (?) Is cupric-ion present? To another portion add ammonium hydroxide (?)

How do double salts differ (a) from complex compounds like potassium cuprocyanide and ammonio-cupric sulphate and (b) from simple salts like cupric sulphate?

**174. Equivalent of Copper [Quant]** Take a small rod of pure zinc, smooth the ends with a file, and weigh carefully Place in a beaker an exactly known weight of crystallized cupric sulphate (about 2 g), and dissolve in distilled water

Put the zinc in this solution, and allow them to remain in contact until the latter is completely decolorized. Remove the zinc, free it carefully from the brown deposit (?), and dry and weigh it. What weight of zinc has gone into solution?

To avoid weighing the precipitate of copper, which it would be difficult to do exactly, calculate from the formula what quantity of copper was contained in the amount of blue vitriol taken (?). Calculate from your data the weight of copper displaced by the equivalent weight of zinc found in 23 or 25 *a*, or, if zinc was not then employed, assume the latter to be 32.7. This weight of copper will be the equivalent (that of oxygen being 8). Look up the specific heat of copper (Appendix III), and use this and the equivalent observed to find the atomic weight (?).

What other atomic weights could be measured on this plan?

#### 175 Reactions of Silver Salts

*a* Take 1-2 c.c. of silver nitrate solution. Test its reaction towards litmus [R 437] (?). Is silver more or less active as a metallic element than copper?

Add dilute hydrochloric acid until no further precipitation occurs (?). Filter, wash the precipitate with water, and place a small part of it in the sunlight (?). Reserve the rest for *b*, *c*, and *d*.

Place a drop of silver nitrate solution on the skin, and examine after an hour (?).

*b* To a small part of the precipitate from *a* add ammonium hydroxide (?). What complex ion is formed? Now add dilute nitric acid in excess (?). Formulate the action of this acid (?).

*c* To another small part add sodium thiosulphate solution (?). Pass hydrogen sulphide (see *f*) through the mixture (?). Explain both actions (?).

*d* Place the rest of the precipitate in a porcelain crucible, put on it a piece of granulated zinc, and fill up with dilute sulphuric acid. Stir from time to time (?). After an hour or two

pour off the acid, take out any unchanged zinc, wash the precipitate with water by decantation, add ammonium hydroxide, and filter. Find out whether any silver chloride had remained unchanged and so passed into the filtrate (175 b) (?). When the filter paper is dry, place the dark powder in a hollow on a stick of charcoal and melt it with the flame of the blast-lamp directed downward upon it (?).

e Dilute a few drops of silver nitrate solution and divide into two parts. To one add potassium bromide solution (?), and to the other potassium iodide solution (?). Add to each some ammonium hydroxide (?). Compare the rates of action with that on silver chloride (?). Arrange the three salts and ammonio-argentic-ion in the order of decreasing ability to give argentic-ion (?). Relate this order to that of solubility (Appendix IV).

f Dilute 2-3 drops of silver nitrate solution and lead in hydrogen sulphide (?). Is this action reversible, theoretically? Divide the product into two parts, and to one add dilute nitric acid (?).

To the other part add potassium cyanide solution [CAUTION! POISON] (?). What is formed? Could silver chloride be precipitated from this solution (64 b)? Explain (?).

g Touch Congo-red paper [R 258] with a dilute acid (?) and with a dilute solution of a base (?).

To 1 c.c. of silver nitrate solution add a few drops of potassium dichromate solution (?). Test the solutions before (?) and after mixing (?) with Congo red paper [R 258]. (If the color of the dichromate obscures that of the Congo red, wash the test-paper with distilled water.) What product does this show? Make the equation accordingly (?).

Note that chromic acid solution is deep red in color, and as an acid is too feeble to affect this indicator.

## CHAPTER XXV

### MAGNESIUM, ZINC, CADMIUM, MERCURY

**176 Magnesium** Mix thoroughly in a mortar equal bulks of magnesium powder and powdered calcium carbonate. Put the mixture in a test-tube (it should fill about half an inch of the tube), fix the tube in a clamp on the stand, and heat the top layer in the Bunsen flame until the reaction begins. [CAUTION! Be careful to keep the tube directed away from the face during the heating.] Allow the test-tube to cool, add a little water, and then, slowly, an excess of concentrated hydrochloric acid (?). (If the tube has been broken, place the contents with the acid in a beaker.) Note the odor (?). What effect will the acid have upon any excess of either of the ingredients? The acid will also dissolve the oxides of magnesium and calcium formed by the action. When all action has ceased, filter and wash the black residue (?) with water. After drying this on the radiator or water bath, prove that it is carbon.

This may be done by placing some of it in a dry test-tube, adding a pinch of potassium chlorate, heating in the Bunsen flame, and pouring the gas when it has cooled (close the tube with the thumb while waiting for this) into a test-tube containing 2 c c of limewater, and shaking (?).

What is the reducing agent in this action (par. 1)?

Examine the test-tube (?) and explain [R. 425]

#### **177 Properties of Magnesium Compounds**

*a* Try whether magnesium chloride dissolves completely in water (?). Test the solution with litmus and draw an inference(?).



Heat some of the crystals strongly in a dry test-tube (?) Test the reaction towards litmus paper of the water which condenses in the tube (?), and then remove the liquid from the sides of the tube with a piece of filter paper. Does the residue dissolve completely in water? Explain (?)

*b* To some diluted magnesium sulphate solution add ammonium hydroxide (?) Explain the result in terms of the ion-product constant [R 479] (?) Calculate the value of the ion-product constant, showing all steps in the calculation (?)

Now mix with some ammonium hydroxide several times its volume of ammonium chloride solution (what effect will this have on the ionization of ammonium hydroxide? Would ammonium sulphate answer as well?), and then add the mixture to a new portion of magnesium sulphate solution (?) Explain in terms of the ion-product constant (?)

To this combination of three solutions add sodium phosphate solution (see 117 *c*) (?) Explain the purpose of each ingredient

*c* To a fresh portion of the diluted magnesium sulphate solution add ammonium carbonate solution, and warm (?) Repeat, adding excess of ammonium chloride solution to the magnesium sulphate solution before using the carbonate (?)

Calcium-ion (160 *d*), strontium-ion (163 *b*), and barium-ion (164 *b*) were also precipitated by ammonium carbonate. Repeat *c* with one of them, adding first excess of ammonium chloride solution (?) If you had a salt of magnesium mixed with a salt of one of those other metals, how should you proceed so as to precipitate a compound of the alkaline earth metal first and one of magnesium afterwards?

*d* Add two drops of hydrochloric acid (why?) to about 250 c.c. of the city water, evaporate to small bulk, and test it for calcium-ion and magnesium-ion

*e* Pass hydrogen sulphide through magnesium sulphate

**178. Reactions of Zinc Salts** Use diluted zinc sulphate solution

*a* Test the solution with litmus paper (?) Explain (?)

*b* To a part of it add sodium carbonate solution (?) Bring the contents of the tube to the boiling-point, filter, and wash the precipitate with water. To a portion of the precipitate add an acid (?) Dry the rest of the precipitate for *c*

*c* Heat the dried, basic zinc carbonate from *b* in a porcelain crucible to redness for a few minutes. Remove a small portion of the product and try the action of an acid upon it (?) If it effervesces, ignite for a longer time. What is the color of the final product when hot, and when cold? Reserve for *d*

*d* Moisten the residue from *c* with a drop of a cobalt chloride solution and heat again (?)

*e* To another part of the zinc sulphate solution add a very little sodium hydroxide solution, and shake (?) Filter, suspend the precipitate in water, and divide into three parts

To one add an excess of sodium hydroxide solution (?) Does this show zinc hydroxide to be basic, or acidic?

To the second portion add dilute hydrochloric acid (?) What sort of hydroxide does it now seem to be? Explain [R 529] (?)

To the third portion add ammonium hydroxide (?) What complex ion is formed [R 529]?

*f* To a third portion of zinc sulphate solution add ammonium sulphide solution (?) Filter, and wash the precipitate and filter-paper with water until no odor of hydrogen sulphide remains. To a part of the precipitate add a drop of hydrochloric acid (?) Odor? Preserve the rest of the precipitate for *g*

*g* Roll up a small part of the filter paper from *f* (or *b*) into a ball, and coil the platinum wire tightly round it. Roast the whole in the Bunsen flame (?) Moisten the ash with cobalt chloride solution and heat again (?)

**179 Relative Activity of Several Acids** In clean test-tubes place equal volumes of (1) zinc chloride, (2) zinc sulphate, and (3) zinc acetate solutions. Compare their reactions towards litmus and towards Congo red paper [R 437] (?). Into each pass hydrogen sulphide to saturation (test? Note 37, p. 86) (?). Are actions like this reversible, theoretically? The reverse action consists in the action of what acid upon what insoluble salt in each case? Will it be equal with different acids [R 272, 537-8]? If not, the most active acid will have kept the most zinc in solution and the least active the least. To ascertain how much zinc remains in each solution, filter the mixtures separately and, after testing with Congo red paper (?), add ammonium hydroxide to each (?). The precipitates are zinc sulphide (why?). Compare the amounts (?). Infer the relative activities of the acids (?).

Why was ammonium sulphide used in 178 f?

**180 Ionic Equilibrium** Take a larger amount of zinc sulphate solution, and add dilute sulphuric acid to it cautiously (only a few drops are required) until a sample just ceases to give any precipitate with hydrogen sulphide. Explain (?). To half of the mixture add much powdered, anhydrous sodium sulphate, stir until it has dissolved, and test a part with hydrogen sulphide again (?). What effect must the great addition of sulphate-ion have upon the hydrogen-ion introduced by the sulphuric acid? Why is zinc sulphide now precipitated?

• To the other half of the mixture, add solid sodium acetate and shake until the latter has dissolved. Now lead hydrogen sulphide into the liquid (?). Explain why zinc sulphide is now precipitated (?).

**181 Reactions of Cadmium Salts** Use diluted cadmium sulphate solution

a Same as 178 c. Answer the same questions

b Saturate with hydrogen sulphide (?). Is the action easily reversible? Add dilute hydrochloric acid (?).

By what reactions could you distinguish between salts of magnesium, zinc, and cadmium?

**182 Unknown Substances** Apply to the instructor for three unknown substances. To identify the anions, follow the outline of work in 165. To identify the cations, employ the scheme commonly used in analysis [R 537]. Present to the instructor a logical and coherent, written report, as directed in 165 (?).

**183 Mercurous Nitrate** Place about 10 g. of mercury with 15 c.c. of diluted (1 : 1) nitric acid in a small beaker, and let the action go on for an hour. Stirring will cause crystallization. Dissolve the crystals in water to which a few drops of nitric acid have been added (why?). Use this solution in 185.

**184 Mercuric Nitrate** Boil some mercury or mercurous nitrate with excess of concentrated nitric acid. Evaporate [Hood] the solution on a water bath, moisten with nitric acid, and dry.

**185 Reactions of Salts of Mercury** Use diluted portions of mercurous nitrate solution and of a diluted solution of any mercuric salt, and add to each the following reagents. Compare the results in each case.

- a* Litmus paper (?) Explain (?)
- b* Dilute hydrochloric acid (?) Treat the precipitate, if there is any, with ammonium hydrosulfide [R 536] (?)
- c* Sodium hydroxide solution [R 534] (?)
- d* Ammonium hydroxide [R 536] (?)
- e* Hydrogen sulphide to saturation [R 535] (?)
- f* Potassium iodide solution (shake), until there is no further change (?). What complex ion is formed? Using this solution, try an experiment to show that mercuric sulphide gives an even smaller concentration of mercuric-ion than does this complex ion (?).
- g* Stannous chloride till there is no further change [R 534] (?)

h A clean piece of copper (?) Determine whether any copper goes into solution (?) Explain (Appendix VII)

i Heat a little of a salt of mercury in a dry test-tube (?)

j How could you distinguish a solution of a mercurous and of a mercuric salt, respectively, from salts of silver, copper, magnesium, zinc, and cadmium?

k Do magnesium, zinc, cadmium, and mercury exhibit the properties of typical metallic elements [R 436]? Explain (?)

**186 Couples** Take four pieces of granulated zinc and clean them by placing them in dilute hydrochloric acid in a beaker. After two minutes, pour away the acid and wash the zinc repeatedly with distilled water. Take three test-tubes and place in each 1 c c of one of the following solutions: mercurous nitrate, silver nitrate, and cupric sulphate. Put one of the pieces of zinc in each test-tube (?), and reserve the fourth piece.

Place 2 c c of dilute sulphuric acid in each of four test-tubes. Now wash the three pieces of zinc repeatedly with water and place one piece in each of the four test-tubes of sulphuric acid, taking care to distinguish each piece from the others (?). Which piece acts upon the acid most vigorously (?) and which least so? Explain [R 549] (?)

**187 Concentration Cell** Suspend a rod of tin about 60 mm long by a thread from one end, and hang it near the bottom of the graduated cylinder. Pour in through the dropping-funnel, which must reach the bottom of the cylinder, first water containing 5 drops of dilute hydrochloric acid and then diluted (1:1) stannous chloride solution. Perform the operation with care, in such a way that the solutions do not mix, the dilute acid being finally uppermost, and that the surface at which they meet is near the middle of the rod of tin. If the second solution is permitted to carry air bubbles with it, mixing will inevitably occur. Place the arrangement where it will not be disturbed, and examine from time to time (?) Explain [R 550]

## CHAPTER XXVI

### ALUMINIUM, DYEING, TIN, LEAD

#### 188 Aluminium

*a* Record here the action of aluminium on hydrochloric acid (18 *a*) and its degree of intensity (?) Try the action of the metal on dilute sulphuric (?) and dilute nitric acids (?) Compare and explain (?)

*b* Place some aluminium turnings with sodium hydroxide solution in a beaker (?) To ascertain whether anything has gone into solution, neutralize one-half of the liquid very carefully with dilute hydrochloric acid (?) Test the precipitate by 189 *f* (?)

*c* To the rest of the liquid from *b* add calcium chloride solution (?) To what group of minerals do compounds allied to this belong [R 557]?

**189 Reactions of Aluminium Salts** Use portions of diluted aluminium sulphate solution

*a* Test the solution with litmus paper (?) Explain (?)

*b* Add ammonium sulphide solution (?) Filter off the precipitate, wash it until odorless (why?), and ascertain whether it is a sulphide or not (?) Preserve a part of it for *f*

*c* Add sodium carbonate solution (?) Filter off the precipitate, wash it until free from sodium carbonate (why?), and ascertain whether it is a carbonate or not (?)

*d* Add a little sodium hydroxide solution (?) Proceed exactly as in 178 *c*, and answer the same questions (?) Explain the difference in behavior observed (?)

*e* To a small portion of the suspension from *d* add sufficient sodium hydroxide solution to redissolve the precipitate Then

add excess of ammonium chloride solution, and boil (?) Explain (?)

f Proceed as in 178 *g* with a small part of the filter paper from *b* (?) (or use the method in 178 *d*)

190 \* Alum Prepare warm, saturated solutions of hydrated aluminum sulphate and ammonium sulphate in approximately equimolecular proportions (calculate amounts required), mix them, and set aside (?) Obtain some large crystals by hanging a thread in the solution. Note the form and taste of the crystals (?)

Dissolve one or two of the crystals, and ascertain by experiments selected from 189 whether the solution contains aluminium-ion (?) Infer whether this is a double salt, or a salt giving a complex ion

191 Dyeing Preparing the Cotton In case the sizing has not been removed from the cotton cloth, boil seven pieces in 50 c c of water containing 2 c c of concentrated hydrochloric acid. Rinse the goods in water, dip in 50 c c of cold water containing 0.5 c c of ammonium hydroxide, and rinse again.

Use one piece in 192, two pieces in 194, two in 195 *b* and two in 195 *c*

192 Chrysophenin, a Direct Dye on Both Cotton and Wool To 20 c c of water in the evaporating dish add 5 c c of the chrysophenin suspension\* (shake the bottle) and 1 c c of sodium sulphate solution, and heat to boiling

a Place in this bath one piece each of flannel and of cotton and keep them in motion with a glass rod for two minutes. Remove them and wash in running water (?) Is the dye fast to washing on both? What was the purpose of the sodium sulphate [R 565]?

Smooth out the samples on a square of glass (or a bottle) to dry, and paste them in your note-book

\* Chrysophenin suspension, 1 per cent. Sodium sulphate solution, 8 g  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  per liter

**193 A Lake** Take some cochineal solution, add to it a few drops of ammonium hydroxide, and shake. Then add 1 c c of aluminium sulphate solution, shake, and allow to stand (?)

**194 Alizarin, a Non-basic, Mordant Dye** In a test-tube dilute 2 c c of aluminium sulphate<sup>\*</sup> solution with 10 c c of water, place in it a piece of cotton cloth and boil for two minutes.

In a second test-tube dilute 1 c c of ammonium hydroxide with 10 c c of water. Wring the piece of cloth, place it in this solution and warm and shake for two minutes. Then wring the cloth, which is now mordanted with aluminium hydroxide.

In the evaporating dish put 50 c c of water and 5 c c of the alizarin suspension (shake the bottle). Place in this the piece of mordanted cloth and a piece of unmordanted cotton, and heat to boiling. Keep the pieces of cloth in motion for at least ten minutes. Finally, wash them in running water (?). Is the dye fast to washing on both? Why do they differ [R 565]?

Dry the samples on glass and paste them into the note-book.

#### **195 Basic, Mordant Dyes**

*a* Measure into as many large test-tubes the following solutions

- (1) 2 c c Malachite green (0.05 %)
- (2) 2 c c Methyl violet (0.05 %)
- (3) 2 c c Tannic acid (1%)
- (4) 2 c c Tartar emetic (1%)

Add to each 20 c c of distilled water, and label and number the tubes.

*b* Place two pieces of cotton cloth in the evaporating dish, add the contents of (3), and keep at the boiling-point for five minutes. Wring the pieces of cloth and place them in (4), which is cold, and keep them in motion for five minutes. Then

<sup>\*</sup> Aluminium sulphate, *N*-solution. Alizarin suspension, 5 g. of 20 per cent paste to 100 c c of water.



remove and wring the cloth, which is now mordanted with antimony tannate (?)

*c The Dye without Mordant* Place in (1) and in (2) one piece each of unmordanted cloth, and keep each solution at the boiling-point for one minute. Wash the samples thoroughly in running water (?) Is the dye fast to washing?

*d The Dye with Mordant* Now place in (1) and in (2) one piece each of the mordanted cotton from *b*, boil each for one minute, allow them to cool, and then wash the cloth thoroughly (?) Is the dye fast to washing? Dry all the samples on glass and mount in the note-book

**196 Tin** Place some tin (gran) in a test-tube with diluted nitric acid (1 acid 10 Aq) and set aside. After 198, examine portions of the solution. Determine whether it contains a salt of ammonium (?), and explain. Determine whether it contains stannic-ion or stannous-ion (?) How does tin behave with concentrated nitric acid (198 *d*)? Explain the difference (?)

#### 197 Halides of Tin

*a Stannous halide* Heat about 1 g of tin with pure, concentrated hydrochloric acid (see 16 *a*) (?) Let the action go on until the acid is nearly exhausted. Warm, to hasten the action, and make sure that an excess of tin is always present. Use the solution in *b*, and in 198. Proceed with later experiments until it is ready

*b Stannic halide [Hood]* To one-half of the solution from *a* add bromine-water until the color ceases to be destroyed, and drive off the excess of bromine by warming (?) Use this liquid in 198

**198 Reactions of Stannous and Stannic Salts** In *a*, *b*, and *c* use a portion of each of the solutions from 197, after dilution, with each reagent. Compare the two results in each case

*a Saturate (test?)* each portion with hydrogen sulphide (?) To part of each product add dilute hydrochloric acid, to learn whether the action is easily reversible (?) Filter the remainder

of each product, and treat the precipitates, separately, with warm yellow ammonium sulphide solution [R 572] (?) To the resulting liquids add dilute hydrochloric acid (?) Explain why both give the same product (?) What is the gas evolved?

*b* Add mercuric chloride solution, at first a little and then in excess, first to the stannic (?) and then to the stannous solution (?) When the changes (two) in the latter are complete, boil, let the precipitate settle, filter the clear part of the liquid, and determine whether the tin in the filtrate is now stannous or stannic by adding a drop or two of bromine-water (see 197 *b*)

*c* Add to each portion a little sodium hydroxide solution (?) Proceed exactly as in 178 *c* and answer the same questions (?) Explain the difference, if any, in behavior observed What other hydroxide resembles those of tin and zinc?

*d* Boil a small portion of the stannic solution with tin (gran) for several minutes Now add mercuric chloride solution (?) and compare with the results in *b* (?) Account for the change in the stannic-ion (?) What kind of chemical change was this?

**199 Unknowns** Apply to the instructor for two unknown substances Identify them, and report the result, as directed in 182

#### 200 Lead

*a* Dissolve 1 g of lead acetate in 20 c c of water, place in it several pieces of granulated zinc, and set aside for an hour or two After 201, devise a way of precipitating any remaining lead-ion and showing the presence of zinc-ion in the solution (?)

*b* Wash some of the lead from *a* with distilled water on a filter, and see whether it is possible to get washings which show no reaction for lead-ion with hydrogen sulphide (?) Account for what you observe (?)

**201 Reactions of Lead Salts** Use diluted lead nitrate

*a* Test with litmus paper (?)

*b* Saturate (test?) with hydrogen sulphide (?) Is the action easily reversed?

c Add dilute hydrochloric acid (?) Filter, dilute the filtrate with 5-10 volumes of water, and saturate with hydrogen sulphide (?) Explain (?). What other chlorides are "insoluble"?

d Add sodium hydroxide very gradually (?), first a little, then in excess (?) What other hydroxides resemble this one?

e Add potassium iodide solution (?) Boil, filter, and examine the filtrate (?) Infer a property of lead iodide (?)

f Potassium dichromate solution (?) Proceed as in 175 g (?)

g Dilute sulphuric acid (?) What sulphates are insoluble?

#### 202 Lead Dioxide

a Warm and agitate 1 g of minium with 5-6 c c of dilute nitric acid until it no longer changes in color (?) Dilute with water, and filter. Reserve the precipitate for *b* and *c*. Show by tests selected from 201 that lead-ion is present in the filtrate. What theory of the nature of red lead is suggested by this action [R 576]?

b Treat a part of the precipitate from *a* with sodium hydroxide solution (?) Record here the action of hydrochloric acid upon lead dioxide (48 *a*) and explain it (?)

c Allow the rest of the precipitate from *a* to dry, place it in an evaporating-dish, and direct upon it a stream of hydrogen sulphide (?) Explain (?)

d Do aluminium, tin, and lead exhibit the properties of typical metallic elements [R 436]? Explain?

## CHAPTER XXVII

### ARSENIC, ANTIMONY, BISMUTH

#### 203 Arsenic

*a* Heat one particle of arsenic in a hard glass test-tube (?)

*b* Roast a particle of arsenic on a crucible lid (?) Note the behavior and odor (?)

*c* Mix a pinch of pulverized arsenic trioxide with wood charcoal (pulv.) Heat the mixture strongly in a dry test-tube (?) Compare result with *a* (?)

*d* Boil 0.5 g of arsenic (pulv.) with excess of nitric acid [Hood] (?) Compare with 116 *b* Use the solution for 206 *e*

#### 204 Arsenic Trioxide and Arsenious Chloride

*a* Boil 0.5 g of arsenic trioxide with water (?) Test the mixture with litmus (?) Now add sodium hydroxide solution, and boil (?) To what class of oxides does the trioxide appear to belong? Formulate the whole change

*b* Boil 1 g of the trioxide with 2-3 c.c. of concentrated hydrochloric acid (?) To what class of oxides does it appear now to belong? Formulate this change (?) Set aside and examine later (?) What are the crystals [R. 584]? Is this action reversible? Use the solution for *c* and 207

Is arsenic a typical metallic element? Is it a metallic element at all? Give reasons taken from *a* and *b*

*c* Take a small part of the solution from *b* (setting aside the rest), dilute with water, and saturate with hydrogen sulphide (?) Divide into two parts. With one, try whether the action is easily reversible (?) Filter the other and heat the precipitate with yellow ammonium sulphide solution (?) What

other sulphide behaved in this way? Now add dilute hydrochloric acid to the liquid (?) Explain (?) What is the gas evolved?

**205 Arsenites** Use portions of diluted potassium arsenite solution

*a* Add silver nitrate solution (?), then ammonium hydroxide (?)

*b* Add cupric sulphate solution [R 586] (?)

*c* Test the solution with litmus (?) What substances must be present? Saturate with hydrogen sulphide (?)

**206 Arsenic Acid and Arsenates** For *a*, *b*, *c*, and *d*, use portions of diluted potassium arsenate solution

*a* Add silver nitrate solution (?) Add now ammonium hydroxide (?)

*b* Add magnesia mixture (117 *c*) (?) Compare with 177 *b* (?)

*c* Add to ammonium molybdate solution as in 116 *c* (?)

*d* Add 2-3 drops of dilute hydrochloric acid (?) and saturate with hydrogen sulphide (?) Now add excess of concentrated hydrochloric acid and saturate again (?), heating to assist the action (?) Explain (?)

*e* Neutralize the solution from 203 *d* with ammonium hydroxide, avoiding excess, and use tests selected from *a*, *b*, and *c* (?)

**207 Arsine [HOOD CARE! POISONOUS GAS]** Arrange a side-neck test-tube (or small flask), with safety and straight delivery tubes and nozzle, to generate and burn hydrogen. Place in it a piece of chemically pure zinc, and add pure hydrochloric acid. When the air has been displaced (CARE! Test?), light the gas and hold a crucible lid in the flame (?) If there is no deposit, add a drop of the solution of arsenic trichloride (204 *b*), observe the appearance of the flame, and obtain a deposit on the crucible lid (?) What kind of chemical change takes place in the flame (see 78 *b*)? Heat the tube, through

which the gas passes to the nozzle, with a Bunsen flame (? Marsh's test) When these experiments are completed, fill the test-tube with water to stop the action

Apply bleaching powder solution (fresh) to the deposit (?)

Can arsine be made according to the general method considered in 127 *b*? What other hydrides behave like arsine when heated?

### 208 Antimony

*a, b* Proceed as in 203 *a* and *b*, using antimony (?)

### 209 Antimony Trioxide.

*a* Heat 2-3 g of pulverized antimony with concentrated nitric acid in a small flask [Hood] (?) Dilute, filter, wash the precipitate well [Note 39, p 116], dry, and use in *b, c*, and *d* Use a small part to determine whether the product is a nitrate or not (?) What metal behaved similarly when treated with nitric acid? Compare with arsenic (203 *d* and 206 *e*) (?)

*b* Boil a small part with water (?) Add sodium hydroxide solution, and boil (?) What kind of oxide is it?

*c* Boil a small part with hydrochloric acid (?) What kind of oxide is it?

*d* Boil a part with an equal amount of potassium-hydrogen tartarate in 5-6 c c of water (?) Filter, and set the filtrate aside (?) What are the crystals? To answer this question, dissolve some potassium-hydrogen tartarate and test the solution with litmus (?) Later, dissolve some of the crystalline product in warm water and test with litmus (?) Inference (?)

### 210 Antimony Trichloride and Trisulphide

*a* Treat about 0.5 g of antimony trichloride with water (?), and test the liquid with litmus paper (?) Add more water, warm, and ascertain whether the action is reversible by adding drop by drop (shake between drops) concentrated hydrochloric acid (?) When the liquid has become clear add a large amount of water (?) What law is illustrated? Finally, add concentrated hydrochloric acid again (?), and use the solution in *b*

How does this action differ from that of water upon phosphorus trichloride (118 *b*) and upon arsenic trichloride [R 584]? What is the significance of this difference?

*b* Dilute the liquid from *a*, saturate with hydrogen sulphide (?), and proceed as in 204 *c* (?). Answer the same questions (?)

211 *Stibine* Repeat 207, using antimony trichloride (?)

212 *Bismuth* Prepare a match (or splinter of wood) as in 92, and proceed as in 170 *f*, using any bismuth salt (?) What metals are obtainable in this precise way? Could zinc, mercury, silver, and aluminium be so obtained? Explain (?)

### 213. Compounds of Bismuth

*a* Warm about 1 g of bismuth with 8–10 c.c. of diluted (1:1) nitric acid (?) Concentrate to 3 c.c. and set aside [R 591] (?) Compare this result with arsenic (203 *d*) and antimony (209 *a*), and interpret (?)

*b* Proceed as in 210 *a* (first par.), using bismuth nitrate (or the product from *a*) and nitric acid, instead of the salt and acid there employed (?)

*c* Take 1–2 c.c. of bismuth nitrate solution, dilute it, and clear up with nitric acid if necessary Saturate a part with hydrogen sulphide (?), and proceed as in 204 *c* (?) Compare with the sulphides of arsenic and antimony (?)

*d* To the remainder of the solution of bismuth nitrate add sodium hydroxide (?), at first a little, and then in excess (?). Compare this hydroxide with the oxides of arsenic (204 *a*) (?) and of antimony (209 *b*) (?)

Filter off the precipitate, ignite it in a porcelain crucible, and note the color when hot (?) and when cold (?)

214 Do arsenic, antimony, and bismuth exhibit the properties of typical metallic elements? If not, in what respects do they fail to do so?

215 *Unknowns* Apply to the instructor for two unknown substances Identify them as directed in 165 and [R 537], and report the result. Do not use Marsh's test for arsenic

## CHAPTER XXVIII

### FILM TESTS AND MATCH TESTS

#### 216 Metallic Films

a Obtain on small pieces of paper, bearing the names of the materials, a few particles of each of the six substances. Arsenic trioxide, antimony trichloride, bismuth nitrate, zinc sulphate, lead nitrate, and mercurous nitrate. Lower the Bunsen flame to 5 cm height, and reduce the air supply until a luminous tip appears inside the flame. Clean the outside of the evaporating dish and place a little water in it. Take a long, thin, straight fiber of asbestos, dip the point in the water, and touch the arsenic trioxide with the moist end, so as to pick up a few particles.

Hold the evaporating dish in the left hand so that a glazed part of its exterior is close above the luminous tip. At the same moment, with the right hand, insert the point of the asbestos fiber quickly into the luminous tip itself. Place the asbestos fiber beside the arsenious oxide, for use again in 217, and examine the dish (?). Is there a metallic film, or only a dust on the dish (?). Dip a glass rod in dilute nitric acid (in a test-tube) and moisten the film therewith. Does the film dissolve quickly, slowly, or hardly at all? Tabulate the results as shown below.

Repeat with the other five substances, cleaning off the dish, and using a fresh asbestos fiber for each.

SUBSTANCE	FORMULA	FILM DUSTY OR CONTINUOUS	DILUTE NITRIC ACID
Arsenic trioxide			



*b* What reducing substances are present in the luminous tip? Write the equations for the interaction of carbon with each of the oxides, and of hydrogen with each of the chlorides used. What compounds will the two nitrates give when heated? How is metallic zinc prepared from the oxide commercially?

### 217 Oxide, Iodide, and Sulphide Films

*a* Lower the flame still further, so as to concentrate the film on a small part of the dish. Repeat the first part of 216 *a* with the six substances, holding each in the reducing tip, but holding the dish higher up in the flame, so that the metal may be re-oxidized and the oxide caught on the dish. Note the color of each oxide (?), tabulate the results as shown under *e*, and use each oxide for *b*, *c*, *d*, and *e*, before cleaning the dish and proceeding with the next substance.

*b* Take the dish with the oxide film to a bottle containing phosphorus tri-iodide,\* and blow across the mouth of the bottle so that the gas strikes the oxide, converting it into the iodide (color?).

*c* Breathe upon the iodide film heavily once or twice (?). Soluble iodides become invisible, but reappear on drying.

*d* When the iodide film has reappeared, blow across the mouth of the ammonium hydroxide bottle, so that the ammonia strikes the iodide (?). If the color vanishes, watch whether it reappears by re-escape of the ammonia (?).

*e* Blow across the mouth of the ammonium sulphide bottle, so that the hydrogen sulphide strikes the residue on the dish. This converts it into the sulphide (color?).

METAL	COLOR OF		BEHAVIOR OF THE IODIDE WITH		
	OXIDE	IODIDE	MOISTURE	AMMONIA	AM SULPHIDE
Arsenic					

*f* Obtain an unknown, and identify it.

\* In a very small, stoppered w-m bottle put a small piece of white phosphorus and as little powdered iodine. When the reaction is over, or if the phosphorus catches fire, close the bottle. One such bottle will serve for 10-15 students.

**218. Match Tests.**

a Obtain, on small pieces of paper, bearing the names of the materials, a few particles of each of the seven substances—Cupric sulphate, stannous chloride, silver nitrate, lead nitrate, ferrous sulphate, cobalt chloride, and nickel sulphate

Lower the Bunsen flame to 4-5 cm height and reduce the air supply until a luminous tip appears inside the flame. Cut the head off a match, warm one side of a large crystal of washing soda (hydrated sodium carbonate) in the flame, and rub three-fourths of the match-stick with the melted hydrate. Then hold this end of the match in the flame so as to char it. The purpose is to get a thin piece of charcoal saturated with sodium carbonate.

Place a few particles of one of the substances in the palm of the left hand along with two or three times as much anhydrous sodium carbonate. Add a drop of water and with a penknife blade work the mixture into a stiff paste.

Stick a small mass of the mixture on the charred end of the match, and hold it in the luminous tip until the mass fuses.

Break off the charred end of the match in the mortar, add a little water, and grind the material with strong pressure in the mortar. Wash away the charcoal and lighter particles, and examine the remaining heavy particles in a good light, turning the mortar so as to cause them to move about.

b *Copper, tin, silver, lead* These metals, being malleable, will show minute, flat shining discs (?).

If they are colored (?), transfer some of them with the knife to a piece of filter paper. Touch them with a drop of concentrated nitric acid applied with a glass rod and warm cautiously above the flame (?). A green stain indicates copper. Touch now with a drop of ammonium hydroxide (?). A strong blue color confirms this conclusion.

If the discs are silver white, transfer some of them to a watch-glass, add a drop of concentrated nitric acid, and warm gently

above the flame (do not evaporate the acid) A white, insoluble substance indicates tin (?) If the discs dissolve, giving a clear solution, add a drop of hydrochloric acid A white precipitate indicates silver Confirm (175 b) (?) Confirm further by using as in 175 a a solution of the original substance If there is no precipitate with hydrochloric acid, add a drop of sulphuric acid A white precipitate indicates lead (?) Confirm by treating some of the original substances as in 201 d, e

\* c *Iron, cobalt, nickel* These metals give only heavy, grey particles Magnetize the penknife by stroking the blade in one direction with one pole of a magnet Ascertain whether the blade will now attract and hold the particles To make sure that they are not simply held by the water, wipe them off on a piece of filter-paper, allow them to dry, and try whether the blade now attracts them (?) If it does so easily, they are iron

Whether the particles were attracted or not, transfer some of them to a piece of filter paper Moisten them with a drop of hydrochloric acid and warm above the flame (?) A yellow stain indicates iron (?) Confirm by one of the tests for a ferric salt (231 f) Also apply suitable tests (231) to a solution of the original substance (?) A blue stain (while warm) indicates cobalt (?) Confirm by applying the borax bead test to the original substance (235 a) If there was no distinct stain, add a drop of nitric acid and warm A greenish stain indicates nickel (?) Confirm by the borax bead test with the original substance (237 a) (?)

d Repeat with each of the other six substances (?)

e In the case of each of the seven substances taken, make equations, attaching the name to each formula, as follows

- (1) Effect of heating with sodium carbonate (?)
- (2) Effect of heating the product from (1) (?)
- (3) Effect of heating the product from (2) with charcoal (?)
- (4) Interaction with reagents applied in b or c

*f* Obtain [Instructor] an unknown and identify it. Make a careful report, showing negative as well as positive results (?).

*g* If compounds of arsenic, antimony, zinc, and aluminium had been used in this test, state what, in each case, would have been the result (?).

## CHAPTER XXIX

### CHROMIUM, MANGANESE

219. **Chromates** Melt 5 g of potassium carbonate with equal amounts of potassium hydroxide (omit this from the equation) and potassium nitrate (include only oxygen, from this, in the equation) at a low temperature in an iron crucible [Store-room] and stir in (use the reverse end of a file) 5 g of powdered chromite. Heat strongly [Blast-lamp] for several minutes (?). When the mass has cooled dissolve it in a little boiling water. Filter, and add dilute nitric acid to the solution until it is acid (?). Note the change in color (?).

220. **Dichromates and Chromates** Take some potassium dichromate solution and run into it potassium hydroxide solution from a burette till the change in color is complete. A test-tube trial will show the tint to be reached. Concentrate the solution and allow it to crystallize (?). What kind of salt (neutral, acid, basic, double, or complex) is potassium dichromate, essentially? What are the colors of dichromate-ion and of chromate-ion?

221. **Reactions of Chromates** For *a*, *b*, *c*, use diluted potassium chromate solution. What are the ions in the solution?

*a* Acidify a part of the solution with dilute sulphuric acid (?). Concentrate and set aside to crystallize (?).

*b* Recall the actions of hydrogen sulphide (79 *e*), of sulphurous acid (89 *f*), and of hydrogen peroxide (65 *f*), on such an acid solution (?).

*c* Add lead nitrate and barium chloride solutions to separate portions (?).

*d* Repeat *c* with potassium dichromate solution (?). Compare the results and explain (?).

**222 Chromic Anhydride** Make a cold saturated solution of 5 g of sodium dichromate, add to it two volumes of concentrated sulphuric acid in a beaker, and cool (?) Filter through a small plug of asbestos, and dry the precipitate by spreading it on a piece of broken bisque plate [Store in room]

**223 Chromic Oxide**

*a* Pulverize potassium dichromate (10 g) thoroughly with one-fifth its weight of sulphur, and heat with the blast-lamp in a porcelain crucible for fifteen minutes. Grind up the resulting mass in a mortar with water, filter, wash the green residue [Note 39, p 116] (?), and dry it on a radiator for use in 224. Test the filtrate for potassium sulphate (?).

*b* Make a borax bead, dissolve a particle of chromic oxide in it, and note the effects of the oxidizing and reducing flames upon it (?). All chromium compounds give the same result. If chromic sulphate had been used, what would have been the nature of the chemical action?

**224 Chromic Chloride** Mix the chromic oxide, prepared in 223, with one-third its weight of pulverized wood charcoal, make into a stiff paste with some starch, and mold the mixture into little pellets of the size of peas. Cover these completely with a layer of charcoal powder (why?) in a closed crucible, dry them by heating gently with the Bunsen flame, and let them cool before exposing them to the air (why?). Place them in a piece of hard glass tubing. Then connect with a chlorine apparatus and, when the chlorine gas has reached the pellets and completely displaced the air (why?), heat strongly with a blast-lamp. Conduct any superfluous chlorine into a test-tube filled with sodium hydroxide. Describe the substance which is formed, and try its solubility in water and acids (?).

**225 Chrome-Alum** Dissolve 10 g potassium dichromate in water, add the amount (calculated) of sulphuric acid necessary to form potassium sulphate and chromium sulphate, warm and add alcohol (7-10 c c), a little at a time, until the yellow

color has entirely given place to a pure, bright green. The action takes some time to reach completion. Note the odor (?). Set the greater part of the solution aside to evaporate spontaneously. Concentrate the smaller portion on the water bath until crystals appear. Examine the form and color of the crystals from both portions (?). What is the color of their solution in water? What is the color of chrome-ion?

**226 Reactions of Chromic Salts** Make a solution of chromalum. What are the ions in the solution?

*a* Boil a portion for some time [R 603]

*b* To another portion add sodium hydroxide solution, at first a little (?), then in excess (?). Boil [R 602] (?)

*c* Add ammonium sulphide (?). Filter off the precipitate, wash it until odorless, and determine whether it is a sulphide (?)

*d* Add excess of sodium hydroxide solution and then a large volume of bromine-water, and heat (?). Try another portion, using lead dioxide instead of bromine (?). Infer the nature of the action from the change in color (?)

#### **227 Manganates and Permanganates**

*a* Fuse a mixture of 5 g of potassium hydroxide, 2.5 g potassium chlorate (include only the oxygen, from this, in the equation), and 5 g finely powdered manganese dioxide, at a red heat, in an iron crucible [Store room], stirring with the reverse end of a file, until effervescence ceases (?). Add the last ingredient gradually. Treat the mass with a small amount of cold water, decant the clear liquid away from the precipitate, and use it in *b*, *c*, and *d*. What is the color of manganate-ion?

*b* Dilute a part of the clear green solution with a very large amount of water in a beaker (?). If no change should occur, pass carbon dioxide into the diluted solution (?). What is the color of permanganate-ion? How does this substance differ from manganate-ion with respect to composition, valence, and physical properties?

*c* Add a few drops of alcohol, and warm (?)

*d* To the rest add a boiling solution of oxalic acid (?)

*e* Repeat *c* and *d* with potassium permanganate solution, acidified by adding two or three times its volume of dilute sulphuric acid (?)

*f* Recall the actions of hydrogen peroxide (65 *c*), hydrogen sulphide (79 *f*), and sulphurous acid (89 *g*) on acidified potassium permanganate solution (?)

**228 Reactions of Manganous Salts** Use any manganous salt What is the color of manganous-ion?

*a* Borax bead in the oxidizing (?) and reducing (?) flames

*b* Bead of a mixture of sodium carbonate and sodium nitrate on a platinum wire with any manganese compound (?)

*c* To a diluted solution of a manganous salt, add ammonium sulphide (?) Is the product a sulphide?

*d* To another portion add sodium hydroxide (?) Divide into two parts Shake one with air (?) To the other add bromine-water, and warm (?)

**229 Unknowns** Apply to the instructor for two unknown substances Identify them, and report the result Identify the negative radical as in 165 For the positive radical, use the tests in 216, 217, and 218, and then, if necessary, use the system outlined in R 537.



## CHAPTER XXX

### IRON, COBALT, NICKEL

**230. Iron** Recall the preparation of iron from an oxide (20), and the action of the metal on dilute acids (18 a) (?)

#### **231 Reactions of Ferrous and Ferric Salts I**

*a* Borax bead with any compound of iron (use the oxide) in the reducing (?) and oxidizing (?) flames

*b* Recall the action of heat upon ferric nitrate (22) and upon ferric sulphate (22) (?)

Prepare a dilute solution of ferrous-ammonium sulphate [Note 38, p 87] Dilute some ferric chloride solution [Note 41, p 159] Use portions of these solutions, and add to each the following reagents Compare the results in each case

*c* Ammonium hydroxide (?) Shake with an (?)

*d* Potassium ferrocyanide solution (?)

*e* Potassium ferricyanide solution (?) and add much water (?)

*f* Ammonium thiocyanate solution (?)

**232 Reactions of Ferrous and Ferric Salts II Reductions and Oxidations** Use diluted ferrous-ammonium sulphate and diluted ferric chloride solutions

*a* To portions of each solution add ammonium sulphide solution (?) Ascertain in each case whether the action is easily reversible (?) Explain the behavior of the ferric chloride solution [R 636] (?) How could you determine whether the free sulphur was formed before or after the acidification?

*b* To portions of each solution add potassium iodide solution (?) To a little starch emulsion add a few drops of the ferric-potassium-iodide mixture (?)

c Saturate (test?) a portion of the ferrous solution with hydrogen sulphide (?) Explain in terms of the ion-product constant (?) Now add ammonium hydroxide (?) Filter. Wash the precipitate until odorless, and determine whether it is a sulphide or hydroxide (?) Explain in terms of the ion-product constant (?)

d Saturate (test?) a portion of the ferric solution with hydrogen sulphide (?) Filter. What is the precipitate (test?)? Examine the clear filtrate, and determine, by means of tests from 231 d, e, and f, whether ferric-ion or ferrous-ion is present (?) Formulate the action of the hydrogen sulphide (?)

e Boil a portion of the ferric solution with excess of pulverized iron for several minutes. Filter, and at once apply to part of the clear filtrate (color?) tests selected from 231 d, e, and f (?) Formulate the action of the iron.

f To 2 c c of potassium permanganate solution add a large excess of dilute sulphuric acid (?) Add this mixture drop by drop to 5 c c of a dilute solution of ferrous-ammonium sulphate until the pink color is permanent [R 623] (?) Apply to this liquid tests from 231 d, e, and f (?) Formulate the action in terms of ions alone. Which kinds of ionic chemical change have been illustrated here? How could this action be used for estimating iron?

What other oxidizing agents convert ferrous into ferric salts (see 105 f)?

**233 Hydrolysis** Dissolve 0.5 g each of ferric sulphate and ferrous-ammonium sulphate separately in water, and warm very slightly. Observe the tints by looking downward through the solutions at a piece of white paper (?) Test each solution with Congo red paper, compare (?), and interpret the results. Now add some pure sulphuric acid to each and observe the tints again (?) Explain (?) What are the colors of ferrous-ion and ferric-ion, respectively? Which of these allotropic forms of the element is more typically metallic?

**234 Iron-Ammonium Alum**

*a* Weigh 6 g of ferric sulphate into an evaporating-dish. Weigh out an equimolecular quantity (calculate) of ammonium sulphate. Dissolve the salts separately, each in the minimum amount of boiling water, mix the solutions, and set aside (?) Describe the crystals (?) Collect them upon a filter, wash them free from the mother-liquor, and dry with filter paper.

*b* Ascertain (see 231 *c, d, e*) whether iron-alum is a double salt, or a salt of a complex acid (?)

**235 Ferrocyanides and Ferricyanides** Use diluted potassium ferrocyanide solution

*a* Add ammonium hydroxide (?) and compare with 231 *c* (?)

*b* Add ammonium sulphide solution and compare with

**232 *a*** (?) Is ferrous-ion present?

*c* Add biomine-water (shake) in excess, and boil off the superfluous biomine. To a part of the liquid add ferric chloride solution (see 231 *d* and *e*) (?)

*d* To the rest of the liquid from *c* apply the tests in 231 *c* and *f* (?) Is ferric-ion present?

**236 Reactions of Cobalt Salts** For *b, c*, and *d*, use diluted cobalt chloride solution

*a* Borax bead in oxidizing (?) and reducing (?) flames

*b* Sodium hydroxide solution, first a little (?), then in excess, and warm (?) Shake with an (?)

*c* Ammonium sulphide solution (?)

*d* Potassium cyanide solution, first two drops (?), and then in excess (?) Boil the mixture. Add biomine-water (or chlorine-water, or bleaching powder) and then sodium hydroxide solution (?) Compare this with 237 *d* (?)

**237 Reactions of Nickel Salts** For *b* and *c* use diluted nickel sulphate solution

*a, b, c, d* Same as in 236

**238 Unknowns** Apply to the instructor for two unknown substances. Identify them as directed in 229, and report the result

## APPENDIX

### Correction of Barometric Readings

To reduce the reading taken at room temperature (Temp) to the corresponding height of a column of mercury at 0°, subtract the proper number in the second column (Corr'n) from the actual reading in millimeters [See Note 33, p 39]

Temp	Corr'n	Temp	Corr'n	Temp	Corr'n
12	1 6	17	2 2	23	3 0
13	1 7	18 5	2 4	24 5	3 2
14	1 8	20	2 6	25	3 3
15	2 0	21 5	2 8	26	3 4

### II Tension of Aqueous Vapor in Millimeters

Temp	Press	Temp	Press	Temp	Press
0°	4 6	16°	13 5	26°	25 1
5	6 5	17	14 4	27	26 5
8	8 0	18	15 4	28	28 1
9	8 6	19	16 3	29	29 8
10	9 2	20	17 4	30	31 5
11	9 8	21	18 5	31	33 4
12	10 5	22	19 7	32	35 4
13	11 2	23	20 9	33	37 4
14	11 9	24	22 2	34	39 6
15	12 7	25	23 6	100	760 0

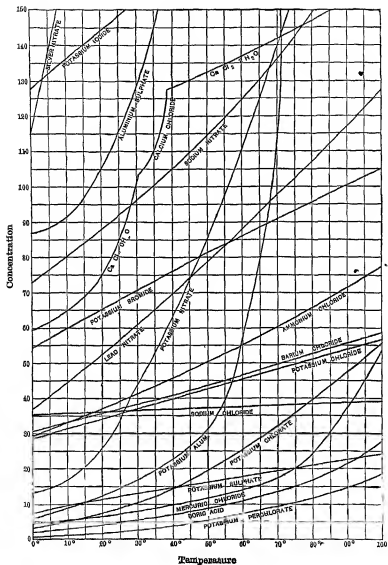
### III Specific Heats of Metals

Aluminium	0 214	Iron	0 114	Magnesium	0 250
Copper	0 095	Lead	0 031	Zinc	0 095

## IV Solubilities of Bases and Salts in Water at 18°.

	K	Na	Li	Ag	Tl	Ba	Sr	Ca	Mg	Zn	Pb
Cl	32 05 3 4	35 80 5 44	77 70 13 3	0 0,10 0 0,10	0 3 0 0,13	37 24 1 7	51 00 3 0	73 10 5 4	55 81 5 1	203 9 0 2	1 18 0 05
Br	65 80 4 0	88 70 0 0	108 7 12 6	0 0,1 0 0,0	0 04 0 0,15	103 6 2 0	06 52 3 4	143 3 5 2	103 1 4 0	478 2 0 8	0 595 0 02
I	137 5 6 6	177 0 8 1	161 5 8 5	0 0,30 0 0,1	0 000 0 0,17	201 4 3 5	109 2 3 0	200 3 8	148 2 4 1	419 0 0	0 08 0 0,2
F	02 50 12 4	4 44 1 00	0 27 0 11	105 4 13 5	72 05 3	0 10 0 0,03	0 012 0 001	0 0016 0 0,2	0 0070 0 0,14	0 005 0 0,5	6 07 0 001
NO <sub>3</sub>	30 34 2 0	83 97 7 4	71 43 7 3	219 4 8 4	8 01 0 35	8 74 0 13	00 27 2 7	121 8 5 2	74 31 4 0	117 3 4 7	51 06 1 4
ClO <sub>3</sub>	6 0 0 02	07 10 0 4	113 4 15 1	12 25 0 6	8 09 0 13	35 12 1 1	174 0 4 6	179 3 5 3	126 1 4 7	183 0 5 3	190 0 3 10
BrO <sub>3</sub>	6 36 0 38	30 07 2 2	152 5 8 20	0 59 0 025	0 30 0 000	0 8 0 02	30 0 0 0	85 17 2 3	42 80 1 5	58 43 1 8	1 3 0 03
IO <sub>3</sub>	7 02 0 35	8 33 0 4	80 43 3 84	0 004 0 0,14	0 050 0 0,10	0 05 0 001	0 25 0 0,57	0 26 0 007	0 87 0 20	0 83 0 02	0 002 0 0,3
OH	112 0 18	116 4 21	12 04 5 0	0 01 0 001	40 04 1 70	3 7 0 22	0 77 0 063	0 17 0 02	0 001 0 0,2	0 055 0 0,5	0 01 0 0,1
SO <sub>4</sub>	11 11 0 62	10 83 1 15	35 04 2 8	0 55 0 020	4 74 0 09	0 0,23 0 0,10	0 011 0 0,6	0 20 0 015	35 43 2 8	53 12 3 1	0 0041 0 0,13
CrO <sub>4</sub>	03 1 2 7	01 21 3 30	111 6 6 5	0 0025 0 0,15	0 006 0 0,1	0 0,38 0 0,15	0 12 0 000	0 4 0 03	73 0 4 1		0 0,2 0 0,5
C-O <sub>4</sub>	30 27 1 6	3 34 0 24	7 22 0 09	0 0035 0 0,2	1 48 0 030	0 0080 0 0,38	0 0046 0 0,20	0 0,50 0 0,43	0 01 0 0027	0 0 6 0 0,4	0 0,15 0 0,5
CO <sub>3</sub>	108 0 5 0	10 30 1 8	1 3 0 17	0 001 0 0,1	4 85 0 10	0 0023 0 0,11	0 0011 0 0,7	0 0013 0 0,13	0 1 0 01	0 0049 0 0,37	0 0,1 0 0,3

The *upper number* in each square gives the number of grams of the anhydrous salt held in solution by 100 c c of water. The *lower number* is the molar solubility, *± e*, the number of moles contained in one liter of the saturated solution.



## VI Degree of Ionization of Ionogens

Except where otherwise specified, the figures give the fraction ionized in a deci-normal, aqueous solution (usually at 18°) Subtraction of the figures from the unity gives the extent to which the ions will unite when brought together in normal concentration At greater dilutions the ionization is greater and the union of ions less

## ACIDS

HNO <sub>3</sub>	0 92	H H <sub>3</sub> PO <sub>4</sub> (N/2)	0 27
HNO <sub>2</sub> (conc)	0 09	H HC <sub>2</sub> O <sub>4</sub>	0 50
HCl	0 92	H HC <sub>4</sub> H <sub>7</sub> O <sub>6</sub>	0 08
HCl (conc)	0 13	H C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> (N)	0 004
HCl (N/2)	0 85	H C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	0 013
H <sub>2</sub> SO <sub>4</sub>	0 01	H HCO <sub>2</sub> (N/10)	0 0217
H <sub>2</sub> SO <sub>4</sub> (conc)	0 01	H HCO <sub>2</sub> (N/25)	0 0221
HBr (N/2)	0 90	H HS (N/10)	0 07
HI (N/2)	0 90	H H BO <sub>2</sub> (N/10)	0 01
HClO <sub>2</sub> (N/2)	0 88	HNC (N/10)	0 01
HMnO <sub>4</sub> (N/2)	0 93	HOH	0 01

## BASES

KOH	0 91	Sr(OH) (N/64)	0 93
NaOH	0 91	Ba(OH) <sub>2</sub> (N/64)	0 92
Ba(OH) <sub>2</sub>	0 77	AgOH (N/1783)	0 30
NH <sub>4</sub> OH	0 013	HOH	0 01
Ca(OH) <sub>2</sub> (N/64)	0 90		

## SALTS

KCl	0 86	Na HCO <sub>2</sub>	0 78
KClO <sub>3</sub>	0 83	Na <sub>2</sub> HPO <sub>4</sub>	0 73
KNO <sub>3</sub>	0 83	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	0 79
K <sub>2</sub> SO <sub>4</sub>	0 72	Na <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	0 69
K <sub>2</sub> CO <sub>3</sub>	0 71	BaCl <sub>2</sub>	0 77
KMnO <sub>4</sub> (N/32)	0 92	CaSO <sub>4</sub> (N/100)	0 64
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (N/32)	0 94	CuSO <sub>4</sub>	0 39
NH <sub>4</sub> Cl	0 85	AgNO <sub>3</sub>	0 81
NaCl	0 84	ZnCl <sub>2</sub>	0 73
Na <sub>2</sub> SO <sub>4</sub>	0 70	ZnSO <sub>4</sub>	0 40
Na <sub>2</sub> CO <sub>3</sub>	0 71	HgCl <sub>2</sub>	(<0 01)

## VII. Electromotive Series

The electromotive force of a cell, in which each of the following metals constitutes in turn the negative pole (and gold, *e.g.*, the positive), diminishes in the order given. The tendency to enter the ionic condition in a solution already containing the same ion in normal concentration diminishes in the same order, and hence the ionic form of each of these metals (in normal concentration) is discharged and the metal liberated by every metal preceding it in the series.

Potassium	Cadmium	Bismuth
Sodium	Iron (Fe <sup>+</sup> )	Antimony
Barium	Thallium	Mercury (Hg)
Strontium	Cobalt	Silver
Calcium	Nickel	Palladium
Magnesium	Tin (Sn <sup>+</sup> )	Platinum
Aluminium	Lead	Gold
Manganese	Hydrogen	
Zinc	Copper (Cu <sup>++</sup> )	

## VIII. Lists of Apparatus

**1 Equipment of Laboratory** These articles are for common use. Those marked \* should be fixed in their places, so that they cannot be removed. The articles in this list, for the care of which no individual is responsible, should be as few as possible.

*Balances:	*Magnet, 218
*Barometer (with thermometer)	Radiators or drying oven
*Blast-lamps and bellows (or air supply)	*Roll of paper smooth, colored:
*Burners fish tail	*Scales and weights:
*Cork press	Spectroscope (Browning's, direct vision,
*Iron mortar and pestle	English make) [Instructor]
Jars for refuse	*Tripod for each blast-lamp
*Lens (on light chain) or microscope	

**2 Supply Room** These articles are given out at the supply room when needed. The student who obtains one of them leaves a signed receipt, and is held responsible for the safe return of the article.

Supply of all apparatus in Lists 3 and 4 to replace breakage	Condensers, with rubber tubing and universal clamp and holder 59, 121 a
Articles, if any, which may be omitted from Lists 3 and 4	Distilling flasks 30 c.c. 59, 104 a b, 121 a
Apparatus for making sulphuric acid, viz., distilling flask with bent neck, Chapman pump, rubber connections and screw clamp Exp 85	Electrolytic cells, 66
Bosque plates 222	Graduated flasks (100 c.c., 500 c.c.), 148 b
Bottles square, 50 c.c. 137	Iron crucibles, 219, 227 a
Bottles, round, 500 c.c. 162	Lead dishes, 61
	Retorts 100 c.c., 104 a
	Round bottom flasks 250 c.c., 83, 124
	Screw clamps, 33, 98
	U-tubes, 155 mm., 54 b, 68 b

<sup>1</sup> Student balance, Varsity model. Becker's Sons, Rotterdam.

<sup>2</sup> To prevent use for writing.

<sup>3</sup> Harvard trip scales, with rider (0-5 g.) to avoid loss of small weights, and weights (5 g.-1000 g.). A small platform spring balance (letter balance form), 0-100 g. grad. in 1 g. for measuring chemicals, in case horn-pan balances are not included in the individual outfits (see below).



**3 Individual Outfit Non-returnable** A copy of this list accompanies each outfit and is checked by the student

- |  |   |
|--|---|
| 1 Clay triangle                              | Puremont paper, pkg., 100 sheets <sup>1</sup> |
| Copper wire, No. 22, 10 ft                   | 1 Platinum wire 3 in., No. 23                 |
| 2 Corks, assorted, small                     | 2 Rubber stoppers, 1 hole, No. 0              |
| 1 File, rat-tail, 6 in                       | 1 Rubber stopper, 2 hole, No. 6               |
| 1 File, triangular, 6 in                     | 1 Rubber tubing, 1 ft. $\frac{1}{4}$ in       |
| Filter paper, pkg., 11 cm                    | 1 Sand bath, 1 in                             |
| Gas tubing, 2 ft.                            | 1 Sponge                                      |
| Glass rod, 4 mm., 2.5 ft.                    | 1 Test-tube brush, small                      |
| Glass tubing, 6 mm., 5 ft. <sup>1</sup>      | 1 Test tube holder                            |
| 1 Horn pan balance, 6.5 in. beam             | 1 Towel (or muslin)                           |
| 1 Litmus paper, box, both colors, 100 strips | 1 Weights, set, 10 mm. to 50 g                |
|  | 1 Wire gauze, 1 X 4 in                        |

**4 Individual Outfit Returnable** A copy of this list accompanies each outfit and is checked by the student. A receipt for the outfit is left at the supply room, and the student is then held responsible for the return or replacement of every article upon the list. Articles marked \* may be transferred to List II or even to List I.

- |  |  |
|--|--|
| 1 Beak, pore, 6 cm                               | 1 Evaporating dish, 7 cm               |
| 1 Bridge, galv. iron <sup>2</sup>                | 1 Evaporating dish, 8 cm               |
| 1 Bunsen burner                                  | 1 Flask, wide mouth, 125 cc            |
| 1 Burette clamp                                  | 1 Flask, wide mouth, 250 cc            |
| 1 Cork borer, with rod, 5 mm. <sup>3</sup>       | 1 Flask, 500 cc, with cork             |
| 1 Crucible tongs                                 | 1 Funnel, 7.5 cm., short stem          |
| 1 Defflagrating spoon, 13 mm. bowl               | 4 Glass squares, 5 X 5 cm              |
| 1 Funnel support, two holes                      | 1 Mortar, 10 cm. and pestle            |
| 1 Iron stand, small                              | 1 * Pneumatic trough <sup>4</sup>      |
| 2 Iron rings, two sizes                          | 1 Sink tube, brass <sup>5</sup>        |
| 1 Pinch clamp                                    | 12 Test tubes, 4 X 0.5 ins             |
| 1 Spatula (horn or glass)                        | 12 Test-tubes, 6 X 0.67 ins            |
| 1 Test-tube rack                                 | 1 Test-tube, 6 X 1 ins                 |
| 6 Beakers, neat tall form, no hp.                | 2 Test tubes, hard glass, 7 X 0.67 ins |
| Nos. 6, 1, 2, 3, 4                               | 1 Test-tube, wide neck                 |
| 1 Bottle, special, 52 oz. <sup>6</sup>           | 1 * Thermometer, stem 6 mm             |
| 1 Bottle, special, 4 oz. <sup>6</sup>            | 1 Thistle safety tube, stem 6 mm       |
| 4 Bottles, wide mouth, 250 cc                    | 1 Tube, hard glass, 1 X 0.67 in        |
| 1 Burette, plain, 50 cc                          | 1 U-tube with side tubes, 6 ins.       |
| 1 Crucible porcelain, No. 6                      | 1 Watch glass, 2 ins                   |
| 1 Cylinder graduated, 100 cc                     | 1 Watch glass, 3.75 ins                |
| 1 Dropping funnel, 60 cc stem 6 mm. <sup>7</sup> | 1 Watch glass, 4.5 ins                 |
| 1 Evaporating dish, 5.5 cm                       | 1 Wing top for buret <sup>8</sup>      |

## IX List of Chemicals

All chemically pure, excepting where otherwise stated

After omissions, if any have been determined upon, the substances (excepting those marked Cal) are numbered consecutively and, if a side-shelf is used, their bottles and places on the shelves are numbered to correspond

<sup>1</sup> Stems of dropping funnel, thistle tube, and thermometer are of same diameter (6 mm.) This saves boring fresh corks and thus avoids waste of time and supplies

<sup>2</sup> Substitute for paper in list No. 1

<sup>3</sup> Earthenware vessels,  $\frac{1}{2}$  gallon milk pans for which bridges of galvanized iron can be made, are inexpensive and last longer than tin troughs. The sink if in the desk, can be provided with a tube to slip over the exit and be used for collecting gases

<sup>4</sup> Cork borers, if supplied for common use are abused and soon become worthless. One size suffices

<sup>5</sup> Mouth to fit No. 6 stopper

<sup>6</sup> This dropping funnel is indispensable only in experiments 84 b and 155 a, although very useful in many others

(Spec) indicates a small amount, or **specimen**, of the dry substance. These substances are *used* only in solution.

**Cal** indicates one of the substances in the **calendar** which are set out only when needed, and then on a special shelf. This mark appears also upon the bottle, taking the place of the serial number.

**Numbers in heavy type** (*e.g.*, 20) appear opposite substances which are used in only that one experiment. Omission of the one experiment permits removal of the substance from the list.

**Concentration**, in case of a solution, is given as  $N$ ,  $\frac{1}{2}N$ , etc., to assist students in using suitable proportions in a rational way. The number in parenthesis following the concentration is the weight of the substance required, with water, to make one liter of the solution. Sat = saturated. Excepting where a formula is given, the calculation assumes the use of the commonest form, often a hydrated one.

\*Rubber stoppers, the rest glass.

The labels should bear the name of the substance and all the data mentioned above. Thus both the student and the person who prepares the solution are fully informed as to the nature of the contents.

### Solids

1	Acid borac (spec)	31	Calcium chloride, gran
2	exalt. com'l	42	fluoride pulv 61, 144
	oxalic Cal, 149 b	33	oxide [Quicklime]
3	tartaric (spec.)	34	phosphide 114
	Albumin, brd, Cal, 115 c 116 a 117 c	35	sulphate, pulv, 88 a 163 d
	139 f	36	sulphate [Gypsum], transp. cryst., 30
	Almonds crushed Cal, 139 g	37	Calcium colored
	Apple slices Cal, 89 h	38	Charcoal, animal, pulv, 188 c
4	Aluminum filings	39	wood pulv
5	oxide, purif 20	40	wood splinters 6 X 6 X 50 mm
6	sulphate, hydrated	41	Chromite, pulv, 219
7	Ammonium carbonate, 153	42	Chromium-potassium sulphate [Chromalum]
8	chloride com'l		Cloth cheese Cal, 141 a
9	nitrate 109		cotton white Cal, 191-195
10	molybdate (spec)		woolen Cal, 192
11	oxalate (spec)	43	Coal, bituminous, 134
12	phosphate 152 a	44	Cobalt chloride
13	sulphate	45	Cochineal (apic)
14	thiocyanate (spec)	46	Congo red paper
15	Antimony, com'l	47	Copper foil, 77 a
16	trichloride, 210 a, 216, 217	48	turnings
17	Arsenic, gran 203	49	Cupric bromide, 63
18	triiodide, pulv, com'l, 137 a 216, 217	50	chloride 68 b, 166 a
	Asbestos, long fiber, Cal, 216, 217	51	oxide, pulv
19	short fiber 85, 222	52	sulphate, hydrated
	Baking powder Cal, 156	53	Fat, tallow 37 b 136 a, 139 g
20	Barium chloride, com'l	54	Ferric chloride (spec)
21	hydroxide (spec)	55	Ferric oxide com'l, 20, 138 b, 146 b
22	oxide purif 25	56	Ferric sulphate
23	peroxide, anhyd	57	Ferrous ammonium sulphate
24	Bismuth, com'l, 213 a	58	Ferrous sulphate, gran 4 mm
25	nitrate	59	Flour, Cal, 141
26	Bleaching powder	60	Gelatin 102 c
27	Cadmium sulphate (spec)	61	Gunpowder, 8 c
28	Calcium carbide, 127	62	Iodine
29	Calcium carbonate, purif, pulv, 38 a, 176	63	iron filings
30	Calcium carbonate [Marble], gran 4 mm	64	iron nails washed with gasoline, 70 a, 4
			iron, pulv, 15, 77 b, 232 c

65	Iron pyrites, gran 4 mm, 83 b, 88	105	Sawdust, 133 a
66	Iron, wire Cal, 22, 25 b	106	Silica, pulv, com l 142
66	Labels, paper	106	Silver rod Cal, 20
67	Lactose Cal, 139 d	107	Silver nitrate (spec)
67	Lead, gran, purif, 16 a	108	sulphate (spec)
68	Lead, 1 g pieces Cal, 9 a	109	Soda-lime 125
68	acetate 206	110	Sodium, Cal, 49 b
69	dioxide, purif	110	Sodium acetate fused
70	monoxide	111	ammonium phosphosphate (Micro cosine salt)
71	nitrate, com l	112	carbonate, anhyd
72	oxide, red [Minnum], 202 a	113	carbonate, hydrated
73	Magnesia, gran 120 a	114	chloride (spec)
74	Magnesium, pulv	115	chloride [Common salt]
75	Magnesium, wire size No 10 22 c	116	dichromate, com l 222
76	chloride, 161 g	117	hydrogen carbonate
77	sulphate, hydrated 29 c	118	hydrogen sulphate com'l, 88 d
78	Manganese dioxide, pulv com l	119	hydroxide, parif
79	Manganous chloride (spec)	120	nitrate
80	Meat Cal, 189 A	121	nitrate, com l, 101 a
80	Mercuric chloride, 45 a	122	peroxide 65 a 105 d
80	Mercurous nitrate, 185 (unless made in 183), 210 217	123	phosphate
81	Mercury, Cal, 5 a, 183, 184 [with dropper]	124	sulphate anhyd 42, 180
82	Nickel, "reduced" Cal, 21	125	sulphate, hydrated
83	sulphate, 218, 237 a	126	sulphur, com l, 82 a*
83	Paraffin 37 c 51	127	sulphate
84	Phosphorus, red	128	tetraborate [Borax], pulv
84	sodium, Cal, 217, 229, 238	129	thiosulphate com l, 81 c
85	pentachloride, Cal, 118 c	130	Starch
85	potassium bromate (spec)	131	stannous chloride, 218
86	bromide	132	strontium chloride 163
87	carbonate, purif	133	sulphate, pulv 164 d
88	chlorate, com'l	134	Sugar com l
89	chloride, 149 a	135	sulphur, flowers
90	chromate (spec)	136	roll
91	cyanide, 95% (spec)	137	Talc [Talcum] pulv, 143
92	dichromate, pulv, com l	138	Tin grau, com l
93	ferrocyanide (spec)	139	Tin rod 60 mm Cal, 187
94	ferrocyanide (spec)	139	Turmeric paper, 145 b
95	-hydrogen sulphate, cryst (spec)	140	Vanoline
96	-hydrogen tartrate, 165, 209 d	141	Wood splinters, 16 cm Cal
97	hydroxide, purif	141	Wool yarn white, 105 / 139 /
98	iodide	142	Yeast Cal, 151 a
99	nitrate com'l	143	Zinc, gran, com l
100	perchlorate, 32	143	Zinc, pulv
101	permanganate, com'l	143	Zinc I, 2 g pieces, Cal, 22 b, 23, 25 a
102	sulphate	144	Zinc I, rod 30 to 40 mm, Cal, 174
103	Resin, 37 a 137 d	144	acetate (spec)
104	Sand, for sand baths	145	chloride (spec)
104	Sausage, Cal, 189 j	146	sulphate, 216, 217

## Liquids and Solutions

147	Acid, acetic, 6 N (420 c c, 80%)	157	Acid, sulphuric, dil, 6 N (107 c c)
148	boric (1 sat, 3%) [for burns and cuts]	158	sulphuric normal Cal, N
149	hydrochloric cone 13 N	159	tartaric Cal, N (76)
150	hydrochloric, dil, 6 N (467 c c)	160	Alcohol, 95% Cal
151	hydrochloric, normal, Cal, N	158	Albarrin 20% paste 194 (50)
152	nitric, cone, 16 N	160	Aluminum sulphate, 189, N (111)
152	nitric, dil 6 N (382 c c)	160	Ammonium carbonate, 2 N
153	oxalic, 2 N (sat, 120)	161	(78.5 + 300 c c NH <sub>4</sub> OH)
154	picric (20 + 100 c c alcohol)	161	chloride 4 N (213.5)
155	phosphoric, 173 sp gr 46 N	162	hydroxide com l, 7 N
156	pyrogallol, Cal, 99 (278)	163	molybdate + HNO <sub>3</sub> (70 + 180 c c HNO <sub>3</sub> )
156	sulphuric, cone, 36 N	164	oxalate, N (71)

- 165 Ammonium sulphide, yellow ( $\text{NH}_4\text{HS}$  + S)  
 166 thiocyanate *N* (76)  
 167 Amyl alcohol, 185 b  
 168 Barium chloride, *N* (122)  
 169 Barium hydroxide [Barium water],  $\frac{1}{2}$  *N* (sat. 79)  
 170 Benzene, 37 c, d  
 171 Bismuth nitrate, 213, *N* (181 + 80 c c  $\text{HNO}_3$ )  
 Bleaching powder, fresh, Cal (sat.)  
 172 Bromine element, Cal  
 173 Bromine water,  $\frac{1}{2}$  *N* (sat.)  
 174 Cadmium sulphate, *N* (140)  
 174 Calcium chloride, 2 *N* (219)  
 175 hydroxide [Lime water], 04 *N* (sat.)  
 176 Carbon disulphide, com l  
 177 tetrachloride, 37 b, d, 139;  
 Chlorine water, Cal (sat.)  
 178 Chloroform  
 Chrysophanic Cal, 192 (10)  
 179 Cobalt chloride, *N* (118 5)  
 180 Cochineal solution, 133  
 Cotton seed oil, Cal, 136 a, 136 a, b, 136 g  
 181 Cuprio sulphate, *N* (125)  
 Ether, Cal  
 Fehling's sol. Cal, 129, 139, 140  
 182 Ferric chloride, *N* (90)  
 Formaldehyde, Cal, 140 f (10)  
 Gasoline (petrol), Cal, 37 c, d  
 Glucose syrup com l, Cal, 130 b, 131 a, 139 c  
 183 Glycerine com l, 145 c  
 184 Hydrogen chloride, sol in toluene com l (+  $\text{CaCl}_2$  for drying)  
 Indigo solution Cal (1 g indigo carmine), 94 a, 133 c  
 Kerosene, Cal, 138 a  
 Lead nitrate *N* (165)  
 186 Litmus solution neutral  
 186 Magnesium sulphate, *N* (123)  
 187 Malachite green, Cal, 195 (0 5)  
 188 Manganous chloride 223, *N* (90)  
 189 Mercuric chloride,  $\frac{1}{2}$  *N* (sat. 68)  
 190 Mercurous nitrate,  $\frac{1}{2}$  *N* (70 + 4 c c  $\text{HNO}_3$  + Hg)  
 Methyl acetate, Cal, 136 c  
 191 Methyl orange, 157 a, (1) violet, Cal, 195 (0 5)  
 Milk, Cal, 140  
 sugar Cal, 139 d  
 192 Nickel sulphate 237, *N* (131 5)  
 Petrol, see gasoline  
 193 Phenolphthalein (1 + 500 c c alcohol)  
 Phosphorus trichloride Cal, 213 b  
 194 Potassium arsenate [ $\text{KH AsO}_4$ ], 2 *N* (120)  
 arsenite [ $\text{KAsO}_2$  +  $\text{H}_2\text{AsO}_3$  (90)]  
 bromate, 97 c,  $\frac{1}{2}$  *N* (59)  
 bromide, *N* (119)  
 chlorate, saturated,  $\frac{1}{2}$  *N* (sat., 161)  
 chloride saturated 4 *N* (sat., 320)  
 chromate 221, *N* (97)  
 cyanide *N* (65)  
 dichromate com l, *N*  $\frac{1}{2}$  (74)  
 ferrocyanide, 231 c,  $\frac{1}{2}$  *N* (55)  
 ferrocyanide  $\frac{1}{2}$  *N* (53)  
 hydride Cal, 99 (810) \*  
 iodide  $\frac{1}{2}$  *N* (83)  
 permanganate,  $\frac{1}{2}$  *N* (79)  
 207 Silver nitrate,  $\frac{1}{2}$  *N* (12 5)  
 sulphate  $\frac{1}{2}$  *N* (sat., 5 5)  
 208 Sodium acetate, 91 a *N* (136)  
 210 carbonate 2 *N* (106  $\text{Na CO}_3$ ) \*  
 chlorate, sat., Cal, 137, 6  $\frac{1}{2}$  *N* (sat. 692)  
 chloride, sat., Cal, 157, 5  $\frac{1}{2}$  *N* (sat., 322)  
 -hydrogen sulphate, saturated com l  
 212 hydride, 2 *N* (80) \*  
 213 phosphate, *N* (119)  
 214 thiosulphate *N* (124)  
 215 Stannous chloride, 185 g *N* (112 5 + 500 c c  $\text{HCl}$  + Sn)  
 216 Starch emulsion  
 217 Strontium chloride, 163, *N* (133)  
 Tannic acid, Cal, 195 (10)  
 Tartar emetic, Cal, 193 (10)  
 218 Toluene, com l, 56 g  
 219 Zinc acetate,  $\frac{1}{2}$  *N* (59)  
 220 chloride 179,  $\frac{1}{2}$  *N* (34  $\text{ZnCl}_2$ )  
 221 sulphate,  $\frac{1}{2}$  *N* (72)

